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No. 15 March, 1960

Proceedings

of

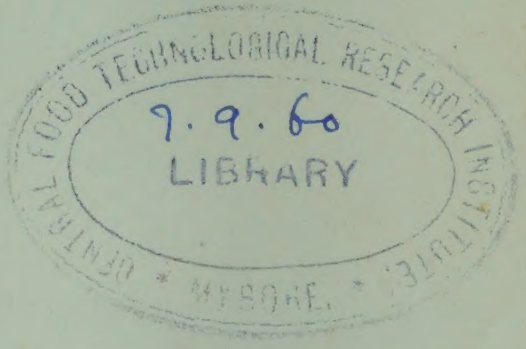
The Symposium

on

VEGETABLE OILS AND THEIR PRODUCTS

held at New Delhi

on October 17-18, 1958



National Institute of Sciences of India

New Delhi

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PREFATORY NOTE

The Council of the National Institute of Sciences of India decided at its meetings held in October 1957 and in March 1958 to hold a symposium on "Vegetable Oils and their Products", and Dr. U. P. Basu, Director of Bengal Immunity Research Institute, Calcutta was appointed the convener to organise it.

The symposium was held on October 17th and 18th, 1958 in New Delhi. Contributions were invited from all the Universities and the Research Institutions interested in the subject, and the response was most encouraging. Altogether 56 papers were contributed and discussed at the symposium. The keen interest that the symposium stimulated was well manifested by the large attendance in the sessions and the lively discussions which followed the reading of each paper.

The Council of the National Institute of Sciences of India takes this opportunity to thank the authors and the participants for their kind co-operation in making the symposium a success.

It is hoped that the publication of the Proceedings of the symposium will be of value and interest to all the workers engaged in researches on Vegetable Oils and their Products.

EDITOR

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INTRODUCTORY REMARKS

Economy of Vegetable Oils & Need for Investigation

by U. P. Basu.

India is essentially an agricultural country with about 70 per cent of her population dependent on land. The agricultural production has been outpaced by the increase in population, and as such the Government of India has launched an all-out drive for agricultural production particularly to make her self-sufficient in food. The pattern of crops grown in India has two striking features: (a) the preponderance of food over non-food crops and (*b*) the wide variety of crops. About 80 per cent of the sown area would be found to grow food crops and these would come to about 270 million acres. Cotton and oilseeds are again the important commercial crops of India. The latter exceeded 30 million acres of sown area in 1957-58 and the production (1957-58) has come upto about 5·9 million tons. The increase as envisaged in the Second Five Year Plan would afford 7,600,000 tons—target in 1960-61. A larger production may help the country in encountering two shortages—one in food and the other in foreign exchange. The symposium on "vegetable oils and their product" is being organised for focussing the attention of scientists, technologists, industrialists and economists towards the above directions.

There are two well-defined crop seasons in India: (*i*) *Kharif* (Autumn) and (*ii*) *Rabi* (Winter). Oilseeds are grown in both the seasons. The main *Kharif* crops are groundnut and sesamum, while the *"rabi"* crops afford linseed, mustard, rape and others. Inspite of these advantages we are far from meeting even the basic needs of fats which our growing population require. An adequate intake of oils and fats is a vital necessity for proper nutrition. An ideal fat-intake is considered to be 20—45% of total calories, or, at least 2 oz. per day. With a rising living standard and widening industrial application of vegetable oils, the *per capita* consumption per year in the world is increasing. It was 11·4 kg. (average) in 1955-56 but there are wide geographical variations (29·4 kg. in North America, 23·8 kg. in Western Europe, 5·1 kg. in Africa and 4·7 kg in Asia). There has been a rise in post-war years consequent on the increase in the output of world oils and fats. The total world production in 1957 excluding U.S.S.R. exceeds 26,000,000 tons. The following tables give an idea on the output and the distribution of production in recent years.

India's production is to be stepped up to keep pace with growing population. Crop production may fluctuate for one or other reason bu the increase in population containues to be relentless. Over and above, industrial development also would demand more oils for one or other purpose. The

output is to be increased and this is a task for which an all-out drive would be necessary.

TABLE I

World Production of fats and oils (in thousand metric tons)

NATURE	1955	1956	1957
Total Edible oils ... ... (Soyabean, groundnut, olive, sesame, cottonseed, rapeseed, etc.)	9,970	10,081	10,890
Total Acid oils (like coconut oil)	2,432	2,571	2,610
Total Technical oils (like castor, linseed)	1,105	1,165	1,408
Fats like butter, lard, tallow ...	11,005	11,415	11,310

TABLE II

Chief Producing Countries (oils in thousands metric tons)

COUNTRY	1955	1956	1957	Export in 1956
U.S.A.	6,215	6,625	6,567	2,182
Western Europe ...	3,638	3,544	3,822	362
China	3,421	3,546	3,703	330
India	2,219	2,046	2,131	162
Eastern Europe	2,014	1,016	1,019	
Phillipines	712	838	870	729
Nigeria	802	902	835	
Argentina	521	648	748	126
Canada	402	524	667	
Indonesia	684	655	655	331
Brazil	517	517	503	

OUR PROBLEMS

The main problem is to increase the production of oils and fats in the country in order to meet all ends. The acreage and production of major oilseeds in India have been elaborately narrated by Dr. Poduval in his interesting article entitled "Importance of Oil seeds, vegetable oils and oil cakes in the Economy of India" (this brochure).

TABLE III

Vegetable Oils (Production, Imports & Exports) in Tons.

Vegetable oils.		1954	1955	1956
Production	...	1,521,149	1,749,767	1,578,025
Import (*a*) free oil	...	51,107	34,240	37,212
(*b*) oil seeds	...	39,337	46,084	53,370
Total oil	...	1,611,693	1,830,091	1,668,607
Export (*a*) free oil	...	64,147	305,869	130,803
(*b*) in the form of oil seeds	...	7,436	18,901	4,965
(*c*) Hydrogenated oil		5,699	15,173	10,863
Total	...	77,282	339,943	146,631
Oils net available	...	1,534,311	1,490,148	1,521,976

The data in Table III would give an approximate idea on the production, import and export figure of vegetable oils of India ,cf. Commerce, 1957, XCV 148).

The Government is aware of the problem of increasing supplies of oil seeds; but the social, technological, economical and industrial complexities are to be encountered for an all round improvement. First of all it may be noted that although total production of oil seeds in India is not low (vide Table II) the amount of land utilised for the purpose is, however, relatively high. It is reported that yields per acre of almost all oil seeds in India are well below the levels as compared to other countries. Before war the average area under cultivation for oil seeds was about 21 million acres. In 1957-58 the acreage has been increased by about 45 per cent to over 30 million acres. The increase in production of oil however has only been 25 percent as the average production before the war was 4·8 million tons. The same in 1957-58 is just over 5·9 million tons. The yield per acre is to be increased 50 per cent whether by selecting high oil bearing seeds, by propagation, by using suitable fertilisers and/or by following improved agricultural practices. This might be possible as it was found that grown in irrigated lands near south Arcot (Madras) yield of groundnut kernels had been increased to 1400 lbs. per acre from the average figure of 450 lbs. Secondly, cotton seeds oil is a good source of edible oil for human beings, but this is being mostly wasted as the cotton seeds (about 1·6 million tons) are being directly utilised as cattle food, and thereby, we are loosing 0·2 million tons of oil. The farmers are to be convinced that cottonseed cake itself is also very rich in protein. Thirdly, the question of extracting oil from the seeds is again a thorny one. This point has been clearly indicated in the Annual Report (1957) of the

Vanaspati Manufacturers' Association of India. In trying to assist the village ghani and in order to offer a gainful employment to our rural population the Government is giving a preference to ghanies over the power mills. If the main objective is to increase total production of oil, the policy must be in favour of efficient processing which is possible in modern extractors. A step in the alternative is to extract out the residual oil from the ghani-cake. For this the esablishment of solvent extraction plants in the country would be an advancement and a redeeming feature, but we would need a good number of plants to treat all the oil cakes that are being produced in the country. This also will lead us to think over a substitute for the present petroleum solvent used for de-oiling oil cakes by the solvent extraction plants as the solvent is being mostly imported. Or, can we conceive of a type of oil expeller that would crush oilseeds in such a way that the oil cake produced might have a much lower content of oil in it. On the other side, we should remember that with development of our animal husbandry we will have to think of better and sufficient feed for our cattle, pig, and poultry. A food rich in protein, carbohydrate, minerals and vitamins would be more in demand. Oil-cake is a good food material. Various questions thus arise. Besides we will have to ponder over the ready supply of fuel for any operative work; or, the containers for one or other processed material. Again various measures and laws have been enacted by the Government of controlling production, distribution or export. The whole are to be adjusted in such a way that the domestic demand for fats and oils is easily met without hindering our export needs to earn foreign exchange. For the latter purpose, we will have to see that the prices of edible oil in India must come down to parity with prices of edible oils in other countries, if we are to increase our exports of vegetable oils and their product and/or to increase their consumption within the country. All these need solution for the national development of the country.

Other Considerations

Vegetable oils are raw materials for various industries, like Vanaspati, soaps, paints, varnishes and pharmaceuticals and as such continuous search for non-edible oils for economic development may be of immense interest to all. In working out with newer type of oils, newer ideas may crop in for better and more economic use of one or other derivatives from the oil. The cake of the seed on one hand and the extracted oil on the others are known to afford a number of industrial products. The former might be converted to give a protein hydrolysate for use in medicine, or, might be suitably treated to afford a yarn for the common man. In processing, in evaluating, in standardising, and in implementation of different ideas, chemists, biochemists, biologists, and engineering technologists will have to take an active part in developing both the basic and applied knowledge.

The oil itself, which is a glyceride, offers one of the most essential raw material (glycerin) for chemical and pharmaceutical industry. Production

of glycerin of high quality is again an art. Different countries have fixed up different standards for pure glycerin and India being an exporting country, it would be of much advantage if a better technique can be developed for the production of glycerin of quality. The other product of hydrolysis of the oil is the fatty acid/s which would have to be still explored to a considerable extent. Numerous derivatives of these fatty acids have lately been utilised in different process industries starting from surface coating agents to complex resin bodies.

There are other uses of oils which many of us are not even so aware of. For example, poppy seed oil is used for the preparation of radiopaques and search in this direction revealed that even our ground nut oil may be a suitable substitute for the same. In investigations with any problem in connection with above objectives in view, newer knowledge will undoubtedly emerge, and as knowledge is the source of power, the symposium would undoubtedly enrich the country and have people with new ideas, thought and enthusiasm.

Conclusion

Number of papers would be placed and discussed. It is to be remembered that in the widely diffused sequence of operations involving growing of oilseed crop, extraction, refining, hydrogenating, hydrolysing or processing the oil or its products, it may be difficult for one specialising in a particular line to appreciate the view-points, needs and difficulties of others. It may be expected that the mutual discussions as envisaged will develop a general appreciation of the diverse problems which confront producers and users of the raw materials and their derivatives from a cash-cum-food crops. Vegetable oil seeds play a vital role in the economy of India. On the one hand it enters into the dietary of the people and on the other, provide raw material for many oil-based industries. If properly and adequately controlled, they are a fairly good foreign exchange earner. It is the duty of the scientists and technologists to find out ways and means in stepping-up of the production to meet all ends. If after discussion, a lead may be given in rational grading of vegetable oils for their different uses on the basis of their availability and actual composition, the objects for which the National Institute of Sciences of India functions, would be fully achieved.

SECTION A
GENERAL SURVEY OF VEGETABLE OILS.

THE IMPORTANCE OF OILSEEDS, VEGETABLE OILS & OILCAKES IN THE ECONOMY OF INDIA—A SURVEY

by R. N. Poduval

Economic & Statistical Adviser, Ministry of Food and Agriculture, New Delhi

Oilseeds, vegetable oils and oilcakes occupy a very important place in the agricultural, industrial and commercial sectors of the Indian economy. Oilseeds serve as the basic raw material for oil-milling industry and thereby provide employment for a large number of people in the urban and rural areas. Vegetable oils constitute the main source of fat supply in the dietary of the people; in addition, they serve as important raw material for industries like vanaspati, soaps, paints and varnishes. Oilcakes provide the much needed nutrition for the cattle and serve as manure for the soil.

The importance of oilseeds in the agricultural economy of India can be visualized from the fact that at present there are about 31 million acres under the five major oilseeds viz. groundnut, sesamum, rape and mustard, linseed and castor seed. Thus, these oilseeds account for about 9% of the total cultivated area in India. The acreage under the five major oilseeds is greater than the area under any other important cash crop such as cotton, jute, sugarcane, spices etc. In addition to the area under the major oilseeds, a sizeable proportion of the net sown area is under a variety of minor oilseeds like coconut, cottonseed, nigerseed, kardiseed, mohwa seed etc.

In the oilseeds economy of the world also, India occupies a very important place. This country is the largest producer of groundnut. In the production of rape/mustard and sesamum she stands next only to China and in that of linseed, India comes next to the U.S.A. and U.S.S.R.

Oilseeds cultivation in the country is confined mainly to the States of Andhra Pradesh, Bombay, Madras, Mysore and U.P. Less important states are M.P., Bihar, Punjab and West Bengal. Cultivation of groundnut is concentrated in Andhra Pradesh, Bombay, Madras and Mysore. Cultivation of sesamum is important in U.P. Rajasthan and Madras. Rape/Mustard is grown mainly in U.P., Rajasthan and Punjab. U.P. and Madhya Pradesh are important in the case of linseed while Andhra Pradesh and Bombay are important for castor cultivation.

Oilseeds cultivation in India has witnessed quite a sizeable expansion in recent years as is apparent from the following table:

Oilseeds	Average 1936-37 to 1938-39	1950-51	1955-56	1956-57	1957-58	1958-59
Groundnut	8,022	11,106	12,685	13,450	14,876	14,481
Linseed	3,736	3,467	3,777	4,156	3,129	3,708
Rape/Mustard	4,269	5,118	6,316	6,311	5,979	6,288
Sesamum	4,068	5,445	5,667	5,446	5,171	5,332
Castor	1,248	1,372	1,418	1,415	1,184	1,193
Total	21,343	26,508	29,863	30,778	30,339	31,002

Total area under the five major oilseeds which stood at 21·34 million acres in the pre-war triennium ending 1938-39 advanced to 26·51 million acres in 1950-51, the base year of the First Plan. In 1955-56, the closing year of the Plan the area under oilseeds increased to 29·86 million acres. The Final Estimates of 1958-59 put the area at 31·0 million acres. In 1956-57 and 1957-58 the acreage under oilseeds amounted to 30·8 and 30·3 million acres respectively. In addition to this, coconut cultivation at present is estimated to be spread over an area of about 1.6 million acres.

Along with acreage, output of the five major oilseeds in the country has also witnessed considerable expansion in recent years, as shown by the data in the following table:—

Production : 100 tons

Oilseeds	Average 1936-37 to 1938-39	1950-51	1955-56	1956-57	1957-58	1958-59
Groundnut	3,145	3,426	3,801	4,200	4,436	4,816
Linseed	428	361	413	384	249	430
Rape/Mustard	733	750	846	1,026	923	1,069
Sesamum	392	438	460	442	354	493
Castor	114	101	123	124	89	111
Total	4,812	5,076	5,643	6,176	6,051	6,919

In 1950-51, the base year of the First Plan, production of the five major oilseeds stood at 50·76 lakh tons as compared to the pre-war figure of 48.1 lakh tons. Five years later, in 1955-56, production advanced to 57·05 lakh tons. In 1956-57 output of oilseeds touched the record figure of 61.8 lakh tons; in 1957-58 a small decline was registered and production stood at 60·5 lakh tons. In 1958-59 production has leapt up to a new record level of 69·2 lakh tons. On the basis of 1958 prices, the value of the oilseeds crop of 1958-59 season will be about Rs. 500 crores.

Though a small portion of the oilseeds crop is consumed directly and a part retained for seed purposes, by far the largest percentage is utilised for extraction of oil. An important by-product of oilseeds crushing industry is the oilcake. Oilcakes are important to our agricultural economy, as they are very valuable as cattle feed. In a country like India which has the largest cattle population in the whole world the value of oilcakes can never be over-emphasized. Oilcakes are also useful for their manurial qualities but utilization in this form is at present being discouraged.

The per capita consumption of edible oils and fats in this country is deplorably below those prescribed by nutritional standards and compares very unfavourably with that of more advanced countries. During 1955-56 the per adult availability of edible vegetable oils for human consumption was about 0·40 oz. per day which, as may easily be seen, is considerably below the nutritional standard (for a well balanced diet) of 2 oz. per day. In 1950-51, the base year of the First Five Year Plan, it stood at the still

lower level of 0·39 oz per day. These facts underline the necessity of increasing production of vegetable oils.

Precise information regarding the utilisation of vegetable oils for various purposes is not available. It is, however, estimated that during 1956-57, of the total produtcion of 14·05 lakh tons of the three major edible vegetable oils (groundnut sesamum and rape and mustard) about 55% was utilised for direct edible use in the form of raw oil. In addition, about 3·3 lakh tons of vegetable oils were consumed by the vanaspati industry during 1957. Thus about 79% of the edible oils produced out of the 1956-57 oilseeds crop was consumed directly or indirectly for edible purposes. This fact highlights the importance of vegetable oils as a source of fat supply in the diet of the Indian people. With the natural increase in population and also with the rising standard of life consequent upon the developmental activity initiated by the Five Year Plans, consumption of oils may be expected to increase in the coming years. To meet this increase in consumption needs it is necessary to step up substantially production of oilseeds.

Important industries using vegetable oils are vanaspati, soap, paints and varnishes and pharmaceuticals. Vanaspati industry at present consumes over three lakh tons of raw vegetable oils. More than 90% of the oil requirements of vanaspati industry are met by groundnut oil. Other oils used are sesamum, cottonseed and coconut oils. Every year the organised sector of the soap industry is estimated to consume about 21 thousand tons of groundnut oil and 25 thousand tons of coconut oil besides small quantities of linseed and rape and mustard oils. About 40 thousand tons of linseed oil are taken up annually by the paints and varnishes industry. Besides, some quantities of sesamum, castor and mustard oils are used for medical and other miscellaneous purposes. Reliable figures of consumption for medical and other purposes are, however, not available. But one estimate puts the figure at 34,000 tons out of which 32,000 tons are accounted for by sesamum and castor oils and the remaining by mustard oil.

In addition to the industries mentioned above which depend on vegetable oils, the oil-milling industry itself occupies a place of importance in the industrial structure of this country. Both from the point of view of the productive capital invested and employment potential, the oil-milling industry deserves special mention. A major part of the oilseeds produced in India, as mentioned earlier, is crushed for oil. The crushing is done either by village ghanis or power-driven mills. There are about 4 lakh ghanis in India; in addition, there are about 8200 mills employing about 82,000 persons. Ghanis are estimated to employ about 5 lakh persons (1956). The installed capacity of the mills is put at 31 lakh tons while that of ghanis at about 20 lakh tons. At present, a significant part of this capacity is unutilised and it is estimated that the maximum employment potential of the existing units in the industry is about 1·2 lakh persons in the case of oil mills and about 7 lakh persons in the case of ghanis. It will thus be seen that the oil-milling industry's employment potential is quite considerable.

About half of the current estimated production of 15-16 lakh tons of the five major vegetable oils in the country is accounted for by the organised mill sector. The importance of oil-milling industry in the organised mill sector may be had from the fact that during 1954 the total productive capital employed in the industry was of the order of Rs. 25 crores. During that year this sector of the industry consumed materials of the value of Rs. 88 crores while the value added by manufacture was 1·20 crores.

In the foreign trade of this country also, oilseeds and their products play quite a significant part. In the past few years some important changes have taken place in the pattern of our export trade in oilseeds, vegetable oils and oilcakes as will be clear from the following table :—

Q-Quantity : 000 tons
V-Value : Lakh Rupees

Commodity	Average 1936-37 1938-39		to 1950-51		1955-56		1956-57		1957		1958		1959 (Jan. to June)	
	Q	V	Q	V	Q	V	Q	V	Q	V	Q	V	Q	V
Oilseeds	1,161	1,559	186	1,530	40	346	—	—	3	17	5	34	23	206
Vegetable Oils	13	63	113	2,222	250	2,992	77	1,245	1,472	1,142	1,055	744	595	418
Oilcakes	380	257	20	3	163	530	56	167	78	217	235	745	205	725
Total		1,879		3,755		3,868		1,412		1,376		1,523		1,349

Formerly oilseeds used to be exported in large quantities but now vegetable oils have taken up their place. This is the result of our export policy which is directed to encourage domestic oil-milling industry. Also it is necessary to conserve our oil cake supplies for internal use. Of late, the domestic demand for vegetable oils also has gone up considerably as a result of increase in population and rising standards of living. Consequently, prices have gone up and exports have fallen in recent years. Compared to the pre-war exports of 466 thousand tons in terms of oil valued at over Rs. 16 crores, exports of the five major oilseeds and their vegetable oils during the period of the first five year plan averaged only at 134 thousand tons. During 1950-51 the base year of the First Plan total exports in terms of oil were of the order of 180 thousand tons valued at Rs. 37.6 crores. Exports in the closing year of the plan i.e. 1955-56 were also substantial, a quantity of 262 thousand tons in terms of oil and the total revenue earned therefrom (including oil-cakes) amounted to Rs. 38·7 crores. There was a heavy fall both in the quantity and value of exports during 1956-57 mainly because of the restrictive export policy followed during the period. The decline in the quantity and value of vegetable oils continued up to the early part of 1958. Since 1958 the policy regarding export of oilseeds, vegetable oils and oilcakes has been relaxed and in the first half of 1959 export earnings in respect of oil seeds, vegetable oils and oilcakes amount to Rs. 13·49 crores as against the total earnings of Rs. 15·23 crores for the whole year in 1958 and Rs. 13·76 crores in 1957.

Export of oilcakes which remained banned for over a decade came to be licensed early in 1955. Towards the closing months of 1954 and early 1955 prices of oilseeds and vegetable oils tended to decline significantly and hence a quota of groundnut oilcake was released for export subject to a heavy duty of Rs. 230/- per ton. This high duty was intended to insulate domestic prices of this valuable cattle feed from an upward pull, exerted by prices abroad. Subsequently other oilcakes also were released for export. Gradually export policy came to be liberalised considerably and exports of some oilcakes were licensed freely without quantitative restrictions and in some cases export duties were either reduced or abolished. However, this liberal policy was reversed in the first half of 1956 consequent on the rise in prices. Revenue received from export of 167 thousand tons of oilcakes in 1955-56 was of the order of 5·30 crores of rupees. During 1956-57 the quantity and value of exports of oilcakes declined to 56 thousand tons and 1·67 crores of rupees respectively evidently because of the restrictive export policy. Recently, liberal quotas have again been released for many oilcakes mainly with a view to augmenting the earnings of much needed foreign exchange.

As has already been stated earlier, there is urgent need of stepping up production of oilseeds in the country with a view to meeting rising internal demand as well as earning more foreign exchange by exporting a part of the increased production. With this end in view, schemes have already been taken in hand. The target of production of the major oilseeds at the end of the Second Five Year Plan has been fixed at 75·5 lakh tons and this is expected to yield about 20 lakhs tons of vegetable oils. An Oilseeds Development Scheme to be implemented by the State Governments in conjunction with the Central Government has been included in the Second Five Year Plan. As no appreciable expansion of area under oilseeds is possible within the country, it is proposed to achieve the target through adoption of intensive cultivation methods. These include multiplication and distribution of improved strains, expansion of research on evolving new and better varieties of oilseeds, application of fertilizers and manures, control of pests and diseases and adoption of improved agricultural methods. Besides these, the Indian Central Oilseeds Committee is also financing schemes for expansion of research on evolving new and better varieties of oilseeds and their distribution. The Indian Central Oilseeds Committee have also launched an Oilseeds Extension Scheme. A Central Supervisory Committee for Planned Production of Oilseeds in India has also been set up. The State Governments have been urged to pay particular attention to groundnut and castor which are important from the point of view of our export trade. Intensive cultivation of groundnut on the pattern of Japanese method of paddy cultivation has been particularly emphasized. Measures contemplated for extensive cultivation are reclamation of waste and fallow lands, double cropping wherever possible and inter-cropping with other suitable crops. It may be expected that as these activities gather momentum out-turn of oilseeds in the country will show substantial expansion.

AREA AND PRODUCTION OF OILSEEDS

Area : 000 acres
Production : 000 tons

GROUNDNUTS.

States	1950-51		1955-56		1956-57		1957-58*		1958-59†	
	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.
Andhra	2,990	1,024	3,064	1,070	3,122	1,124	3,212	1,090	2,649	1,003
Bombay	3,643	842	4,545	1,049	4,700	1,137	5,856	1,347	6,069	1,762
Madras	1,962	751	1,778	821	1,799	854	1,877	896	1,886	908
Mysore	1,575	538	2,035	469	2,221	598	2,132	619	2,036	569
Other States	936	271	1,263	392	1,608	487	1,799	484	1,841	574
Total	11,106	3,426	12,685	3,801	13,450	4,200	14,876	4,436	14,481	4,816

* Partially Revised Estimates and subject to revision.
† Final Estimates and subject to revision.

Area : 000 acres
Production : 000 tons

SESAMUM

States	1950-51		1955-56		1956-57		1957-58*		1958-59†	
	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.
Andhra	782	63	667	52	675	57	655	52	619	55
Bombay	799	66	734	56	692	51	640	52	619	54
Madhya Pradesh	1,006	88	1,073	105	794	67	797	45	838	68
Madras	307	32	360	44	351	44	278	36	287	37
Rajasthan	713	53	962	74	1,183	91	1,095	53	1,207	114
Uttar Pradesh	1,248	83	1,167	68	1,161	77	1,115	62	1,140	106
Other States	590	53	704	61	590	55	591	54	622	59
Total	5,445	438	5,667	460	5,446	442	5,171	354	5,332	493

* Partially Revised Estimates and subject to revision.
† Final Estimates and subject to revision.

Area : 000 acres
Production : 000 tons

RAPE AND MUSTARD

States	1950-51		1955-56		1956-57		1957-58*		1958-59†	
	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.
Assam	313	55	280	51	286	56	295	56	288	60
Madhya Pradesh	301	39	356	59	377	56	230	25	360	53
Punjab	461	74	662	105	707	111	737	116	897	163
Rajasthan	268	35	619	97	657	110	855	116	720	78
Uttar Pradesh	3,069	451	3,697	426	3,667	603	3,195	510	3,262	583
Other States	706	96	702	108	617	90	667	100	761	132
Total	5,118	750	6,316	846	6,311	1,026	5,979	923	6,288	1,069

* Partially Revised Estimates and subject to revision.
† Final Estimates and subject to revision.

Area : 000 acres
Production : 000 tons

LINSEED

States	1950-51		1955-56		1956-57		1957-58*		1958-59†	
	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.
Bihar	267	23	253	27	194	12	139	11	258	29
Bombay	590	48	549	48	592	54	602	53	594	56
Madhya Pradesh	1,248	108	1,420	132	1,714	130	1,045	54	1,293	124
Uttar Pradesh	787	130	881	128	837	111	769	80	892	159
Others	575	52	674	78	819	77	574	51	671	62
Total	3,467	361	3,777	413	4,156	384	3,129	249	3,708	430

* Partially Revised Estimates and subject to revision.
† Final Estimates and subject to revision.

Area : 000 acres
Production : 000 tons

CASTOR SEED

States	1950-51		1955-56		1956-57		1957-58†		1958-59†	
	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.	Area	Prod.
Andhra	957	60	856	62	844	64	662	32	665	47
Mysore	161	17	315	35	314	35	280	25	287	30
Other States	122	8	111	8	112	9	101	9	100	9
Other States	132	16	136	18	145	16	141	23	141	25
Total	1,372	101	1,418	123	1,415	124	1,184	89	1,193	111

* Partially Revised Estimates and subject to revision.
† Final Estimates and subject to revision.

LESSER KNOWN OIL SEEDS

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Need for an increased vegetable oil production.

India is one of the largest edible oil seed producing countries in the world. But the production is not enough to maintain a satisfactory level of fat consumption in human nutrition. The per capita consumption of edible fats and oils in India is estimated at 6·7 lbs. of edible oils and 1·5 lbs. of Vanaspati at present, making a total of 8·2 lbs. (Govt. of India Planning Commission p. 412 ; 1956). The per capita consumption is expected to go up to 8·8 lbs. at the end of the second five year plan, but even then it will be far below the recommended consumption of 2 oz. of fat per day. Hence it is necessary for us to increase our oil seed production to the maximum extent possible.

Vegetable oils and oil cake play a very important part in our foreign trade. The export of "wasting assets" like coal, iron ore, manganese and chrome is not beneficial to the country in the long run. Minerals once mined cannot be replaced. On the other hand the export of agricultural commodities and manufactured goods is more advantageous since they can be produced again. Even after attaining the maximum possible degree of self sufficiency we may have to depend upon imports of strategic materials like petroleum, sulphur, phosphates etc. and oilseeds which are in demand in other countries will always come in handy to finance our imports.

The need for increasing our vegetable oil supply to feed our growing soap and paint industries cannot be overemphasised. A successful export trade in these products can be built up only if there is a plentiful supply of vegetable oils in the country.

The targets for the Second Plan.

Under the Second Plan it is proposed to increase the production of vegetable oils from 1·76 million tons (1954-55) to 2·11 million tons (1960-61) (*loc cit* p. 415). This is to be brought about as follows:

(*a*) an increase in the production of major oil-seeds,
(*b*) developing the cottonseed crushing industry, and
(*c*) large scale adoption of solvent extraction of oil cakes.

No specific targets are sugested as regards the production of oil from minor oil seeds such as Mahua, Neem etc.

Importance of minor oil seeds bearing trees and plants.

The prime necessity of a growing nation is food, and with the continued shortage of the same in the country, any diversion of cultivable area from cereals to oil seeds is not practicable. Intensive cultivation of oil seeds

can be adopted but there are limitations in increasing production by this method beyond a limit. Hence more and more attention has to be paid to the lesser known oil seeds which are available in the country but remain unexploited. The organised collection of the minor oil seeds which now go to waste because of neglect will make a sizable contribution to our vegetable oil supplies. If steps are taken to increase the number of these oil seed bearing plants and seeds, our vegetable oil wealth will increase and the periodic shortage of oil and consequent rise in prices which we are witnessing year after year for the last few years will not get repeated so often if not entirely eliminated.

It is fortunate that oil seed bearing trees like Mahua, Khakan, etc. grow wild in various parts of the country. Perennial oil seed bearing trees like the coconut, palm and the red palm have got an inherent advantage over annuals like groundnut, cottonseed etc. They are much less susceptible to the vagaries of monsoon than the annuals. Once planted and brought up they continue to yield the oil seeds year after year without much effort. No wonder the coconut palm is called "KALPAVRIKSHA" in India. The minor oil bearing seeds like Mahua and Khakan also belong to this category. Like the coconut they are multi-purpose in nature. They yield other products besides oil seeds and in any planned scheme of tree propagation they should find their rightful place. A few of the multi-purpose trees are described below.

Mahua

The three important species of Bassia, Bassia butyraceae Bassia latifolia, and Bassia longifolia grow in India. Bassia butyraceae yields the phulwara butter while the others yield Mahua oil. The trees are propagated from seeds and they commence bearing crops of flowers and fruits when about ten years old. The average yield of a tree is about 150 lbs. of flowers and 100 lbs. of seed. The reported yield of fat on the whole seeds is as follows. Bassia butyracea 43.75 per cent. Bassia longifolia 38.46 per cent and Bassia latifolia 32.42 per cent. In some parts of the country Mahua oil is used for edible purposes also. The oil is used extensively in soap making in India. It has been stated that Mahua trees can be used as host plant for grafting edible Sapota. Thus Mahua trees can yield Sapota-fruits, Mahua flowers and Mahua oil. It would not be an exaggeration to state that each family in India can assure itself of the family's needs of fruits, oil and soap by planting just one or two Mahua trees in the backyard of the house. Bassia butyraceae will be the ideal tree for propagation, if it can be grown in all parts of the country because its growth is more rapid than the others and the fat produced is of a superior quality.

Khakan

Salvadora Oleoides (N.O. Salvadoraceae) and Salvadora persica are the two allied species which yield the Khakan oil or Pilu oil of commerce.

Salvadora Oleoides is a large evergreen shrub or small tree widely distributed in North India and thrives best in semi-desert conditions where the rainfall is below 25 inches. Hence this is an ideal tree for desert reclamation. Salvadora persica grows in wetter regions and is a common tree in the North Canara Coast and the tidal creeks of Thana District. (Cooke, ?)

The Khakan tree (Salvadora Oleoides) bears small rounded fruits about 5 m.m. in diameter resembling currents when dry and having considerable value to the poorer classes as a food stuff. The seeds yield about 42-43 per cent. of yellowish-green fat very rich in lauric and myristic and highly valued for soap making. The crude expressed oil contains about 1·5 per easily removed by deodorisation or steam distillation (Patel *et al.*, 1926). The solvent extracted oil is free from this impurity perhaps because it gets distilled out during steaming out of the solvent.

India is at present importing 40,000 tons of coconut oil costing about Rs. 8 crores to feed her soap industry. By developing Khakan cultivation we can, not only do away with these imports but also develop an export trade. In addition vast areas of semi-desert land can be profitably reclaimed. Since Khakan leaves are eaten by camels and goats the fodder problem for these animals in these regions can be solved by systematic planting of these trees.

Punna. (Polang).

Calophyllum Inophyllum (N.O. Gutti ferae) is a tree growing abundantly on the West Coast of India. The trees come to bearing between 3 and 4 years after planting the seed. An average adult tree may yield about 64 lbs. of fruits in each of the two productive seasons in the year, Feb-May and Sep-Nov. The oil content is about 60 per cent. As the flowers of Calophyllum attract honey bees apiaries can also be established. The tree provides a suitable support for peppervine an important dollar earner. Rightly, the Kerala Government is very enthusiastic about the potentialities of these trees and are actively considering the development of plantations.

The oil contains some resinous matter but this can be easily removed by refining. (Rau and Simonsen, 1922; Joshep and Sudborough, 1922).

Kusum.

Schlei-chera trijuga (N.O. Sapindaceæ) the well known kusum tree is another multipurpose tree with vast potentialities. It is an important host plant for growing the lac insect and it yields a valuable oil seed containing 57-80 per cent. of oil. The oil is useful for soap making and is considered the original MACASSAR OIL renowned as a hair tonic.

Neem and Karanja.

According to available data about 1,66,300 tons of neem seeds (from Uttar Pradesh, Madras and Madhya Pradesh) and 17,000 tons of Karanja Seeds (from Madras and Madhya Pradesh) are available but due to want of organised collection the whole quantity is not utilised for oil production.

Neem and Karanja oils contain, in addition to the natural glycerides, some minor constituents which make the raw oil not quite suitable for making quality soap. But the oils could be subjected to splitting and the distilled fatty acids used for soap making. Alternatively they can be subjected to the various liquid extraction processes which have recently gained prominence.

Pisa.

Actinodaphne Hookeri (N.O. Lauraceæ) is a small tree found on the Eastern and Western Ghats and in Sikkim. Its seed gives an oil and a fat the latter from the kernel and the former from the endocarp. The kernel fat is rich in lauric acid and hence very useful in soap making. The mixed oil obtained from the berries is very dark in colour and hence requires further processing to make it suitable for soap making.

Other Oil Seed Bearing Trees and Plants.

In addition to the trees described above there are a number of other oil seed bearing plants and trees which need our attention. The weed GOKHRU (Lanthium Strumaricum) has gained attention now not as a noxious weed but as a producer of oil seed.

Tobacco seed oil from tobacco seed which was wasted till now has appeared in the market and has found acceptance for industrial purposes.

The other plants which require attention are Moringa species which yield Ben oil, Argemone plant yielding Argemone oil, Walnut yielding Walnut oil, Tea plant as source of tea-seed oil and Stillingia Sebifera yielding Stillingia oil (Aggarwal, 1953).

Need for Planned Development.

Recently our Prime Minister Pandit Jawaharlal Nehru declared that for every tree cut two must be planted. This is a timely advice to be heeded not only by the people in India but also by local bodies and the various Government Agencies. There must be a carefully formulated plan for tree planting and the plan should be religiously put into practice during the Vanamahotsava celebrations. In these schemes of tree planting the oil seed bearing trees serving a multi-purpose should get their rightful place. In this connection the Indian Central Oil Seeds Committee with its vast resources has got an important part to play. A beginning has been made in the form of a Pilot Project survey-cum-collection and utilisation of non-edible oil seeds at an estimtaed cost of 2.05 lakhs of rupees. (*Indian Oil Seeds J.*, 1958). Extensive propaganda must be carried out to educate the public on the advantages of growing oil seed bearing trees and viable seeds must be made available at nominal cost. The co-operation of municipalities and other local bodies and even political organisations must be enlisted in the noble task of ensuring the prosperity of the generations to come.

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DEVELOPMENT OF SOAP INDUSTRY IN INDIA

Its problems and their solutions

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Introduction

Soap has been in use from time immemorial and is the universally accepted adjunct to cleanliness in our daily life. The per capita consumption of soap in India is 1 lb. as against 7.2 lbs. in Japan and 27.8 lbs in the U.S.A., so that it leaves a wide scope for further increase in its use in this country in keeping with the progress of its expanding economy.

The Second Five Year Plan envisages an increase in the national income by 25 per cent with consequent improvement in the general standard of living of the people. Development Projects and National Extension Services will contribute to improved habits of cleanliness in the villages. The provision made in the Second Plan for improving water supply and sanitation in rural and urban areas should also promote better habits of cleanliness of the people. The programme of industrialisation that is now afoot will result in urbanisation of a sizable section of our population. Further, the basic and heavy industries under present construction will lead to multifarious ancillary industries during the third and subsequent plan periods with consequent further increase in urbanisation and in general standards of living. These factors, together with the anticipated increase in population, point out towards a definite increase in demand during the coming years for a variety of consumer goods of which soaps and allied products form an essential part.

Further, the present drive for increasing the export trade of the country will also make its own demands to be met by the soap industry.

The soap industry, like other industries, is therefore passing through a time when it has to solve the many problems of its growth. These problems are more complex because the expanding economy of the nation brings about dynamic changes in the habits of its people which demand changes in the types of the products they consume. For instance, the housewife in a city-flat finds it more convenient to soak the day's wash in soap or synder solution while her village-counterpart continues to rub the soap-cake and beat the clothes beside the village pond or the wayside well. Again, as more people wear rayon, silk and nylon there will be further increase in demand for synthetic detergents. Thus one may presume that as more people drift towards towns and cities and change their habits of dressing and washing there will be new demands for washing chips and flakes and beads and powders including syndets. Simultaneously, as the bulk of the population in villages, industrial suburbs or city 'bustees' starts earning increased wages, the demand for soap bars and cakes will also increase.

Similar shifts in demands are bound to occur in the case of the various products of the industry as a whole.

These changes and developments need detailed consideration at every stage of expansion for which systematic market research will have to be undertaken by the industry. Accordingly new products will have to be formulated for which the existing manufacturing facilities will need requisite modifications.

Further, the techniques for publicity, distribution and marketing of the products will also have to be modified and intensified to reach the different sections of the changing and growing communities. Such efforts are very necessary for promotion of sales without which it will be very difficult to realise the proposed targets as is obvious from the fact that production in the organised sector has increased by only 14% over the last 2 years.

Besides, quality soaps will have to be manufactured at competitive price to promote their exports for which a regular export programme will have to be worked out in co-ordination with the Government.

Expansion of soap Industry

It was estimated that in 1955-56 the soap industry had an overall production capacity of around 3,40,000 tons which were distributed as follows:

1.	Large and small factories of the Organised Section which were registered under the Industries (Development and Regulation) Act: (56 Nos.)	1,99,000 tons
2.	Fairly well organised units in the Cottage Sector (18 Nos.) ...	41,000 tons
3.	Smaller units in the Cottage Sector (number not known) ...	1,00,000 tons
	Total ...	3,40,000 tons

To the above may be added 17,000 tons of capacity proposed to be implemented by 1960-61, by the All India Khadi and Village Industries Association. Thus the total capacity envisaged by the end of Second Plan should work out to nearly 3,57,000 tons of which about 2,00,000 tons may be attributed to the organised sector and the rest to the cottage sector of the industry.

The production of soap in 1955-56 amounted to nearly 2,00,000 tons of which 99,000 tons were manufactured by the organised industry as follows:

	Types		Tons
1.	Washing Soap	...	82,000
2.	Toilet Soap	...	15,000
3.	Medicated Soap	...	300
4.	Others	...	1,700

Against the above, it is estimated in the Second Five Year Plan that the over-all production of soaps in 1960-61 will increase to 3,00,000 tons of which

2,00,000 tons have been allotted to organised sector. However, the organised sector produced only 1,12,704 tons in 1957 and as such it is surmised rather optimistically that this sector may produce around 1,50,000 tons by 1960-61, which can be effectively realised within the present installed capacity. Thus it will require only the active use of the present idle capacity without adding any new capacity to the industry as a whole, although it will necessarily involve transference of idle capacities to some of the factories in the Swadeshi sector to enable their effective utilisation.

While discussing any proposal for expansion of the soap industry in India it becomes necessary to consider its broader implications with regard to the different sectors of the industry. Unlike the set-up of this industry in many other countries or that of many other industries in our own country, the set-up of our Soap Industry is rather peculiar because five distinct groups exist in it. For instance, the cottage industry itself consists of two groups of which one is fairly well organised and the other is disorganised although both are non-power operated and both enjoy the exemption of Excise Duty granted by the Government as their production seldom exceeds 125 tons a year.

The organised (and power-operated) sector itself comprises of three groups which are:

1. The organised, small factories, whose economy is basically unsound in the face of competition from both cottage industry as well as the organised larger factories, whereby they find it difficult to sustain themselves and thus possess a high percentage of idle capacity.

2. The organised larger factories in the so-called swadeshi sector of the industry who also have their own problems in the face of unequal competition from the international combines with the result that a part of their own potential capacity continues to be idle.

3. The so-called international combines which produce around 60 per cent of the total production of the entire organised sector.

Under this set-up the problems of each group or sector are quite specific and need rational solution. It appears that no sector is very clear regarding its share in the future expansion of the industry as a whole although each sector is trying to promote its own interests. Thus the cottage industry is backed up by the Government by virtue of the national policy to encourage small scale industries for the prevention of mass unemployment, while the organised swadeshi industry as such, irrespective of small or big, is represented by the Indian Soap & Toiletries Makers' Association without the participation of international combines in it.

Under the circumstance one starts wondering where this sectarianism will ultimately lead to. Could not the various sectors accept each other and try out a policy of collective progress? At any rate the time has come for the Government to step in—and indeed we are glad they have made a start in this direction by having organised the 'Development Council for Soap'—to consider the following measures along with such other alternatives that the industry as a whole may deem necessary:—

Firstly, the Government may declare the extent to which they want to encourage the cottage industry so that the organised industry may come to know the exact scope for its further development.

Secondly, necessary measures have to be taken to effectively utilise the idle capacity of the smaller units. This may be possible by a process of gradual amalgamation or assimmilation of the uneconomic units by transferring their idle capacity to the larger organised units of the swadeshi sector, provided sufficient goodwill is forthcoming from all quarters. At any rate such a process of assimilation may be scrutinised in detail by the interested parties, for, it also offers a solution to the following problems that are now faced by some of them:—

(*i*) High overhead cost per unit output.
(*ii*) Inefficient and outmoded manufacturing technique.
(*iii*) Lack of equipment for the recovery of by-product glycerine.
(*iv*) Disadvantages in buying raw material and selling finished goods due to inadequate finance.
(*v*) Lack of requisite technical guidance, sales organisation and managerial experience.

Thirdly, a balance has to be established between the widely divergent competitive potentials of the organised swadeshi sector on the one hand and international combines on the other, for which it becomes necessary to permit only the former to increase production until at least such time as its capacity is fully utilised.

And fourthly, equitable distribution of new capacities may be granted to interested factories of the organised sector on the basis of inverse proportion to their installed capacities, say, sometime during the third plan period, when the demand for soap products will be around 80% of the total production capacity of the industry as a whole.

Supply of raw materials

Under the rapidly changing conditions the supply of requisite raw materials at economic price needs detailed consideration. To achieve a production of 3,00,000 tons of soap by 1960-61, it is estimated that the industry will require the following approximate quantities of principal raw materials:—

1.	Oils and Fats	...	1,65,000 tons
2.	Caustic Soda	...	30,000 tons
3.	Rosin	...	15,000 tons
4.	Perfumery materials	...	8,00,000 lbs.

To start with, the adequate supply of caustic soda and perfumery materials have to be ensured for which necessary action may be taken by the Government in view of the present restrictions on their imports.

Further, the problem of fluctuation in oil prices needs careful scrutiny and remedy for which the Government may introduce effective measures.

Requisite action is also necessary to augment the supply of oils for soap manufacture. The present problem of shortage of soap-making oils with resultant high prices is rather severe for the following reasons:—

Tallow is objectionable on sentimental grounds while indigenous supply of solid vegetable fats is too limited.

The hydrogenation capacity for manufacture of hardened vegetable oils is also very limited in view of the anticipated increase in production of vanaspati. It is even more so because every ton of hard oil demands two to three times more hydrogen gas depending on the type of oil that is hydrogenated and the final titre of the hardened fat.

The acute shortage in foreign exchange has resulted in drastic cuts in import of coconut oil and palm oil although they are the principal soap making oils by virtue of their exclusive properties.

Edible oils in general are in short supply and they need conservation particularly when import restrictions and export promotion have also contributed to increased price of these oils.

Under the circumstance, our Government have rightly laid down a wide provision for increasing the output of all vegetable oils in the country although one wonders whether all their targets will be effectively realised. Therefore, it becomes necessary to consider the following supplementary measures, some of which are already under the active scrutiny of our Government, to enable their early implementation to the extent they are feasible :—

1. Commercial production of inedible soft oils like Kapok oil, Nageswar Seed oil, Neem oil, Undi oil, Khakhan fat, Karanjia Oil, Maroti Oil, Rice Bran Oil and Tobacco Seed Oil are to be popularised. A recent symposium held on the subject has drawn due attention of the industry which is encouraging in itself. The potential availability of these inedible oil-seeds has been estimated to be 10 lakh tons from which it is possible to extract 1.5 lakh tons of oil, which when realised even partly, will relieve the undue demand for edible oils in the soap industry.

2. Cottonseed crushing is already being encouraged by the Government which may be given further fillip to the extent that may be possible.

3. Requisite additional solvent extraction plants may be installed to enable the economic production of oil from oil cakes.

4. Basic research may be intensified to solve the technological problems regarding refining and hydrogenation of the inedible oils mentioned above.

5. Necessary new capacity is to be granted to oil refining and hydrogenation factories who are prepared to undertake the manufacture of industrial hard oils so as to enable them to supply these raw materials in a readily acceptable form to the soap industry.

6. The consumption of coconut oil and palm oil may be considerably reduced by popularising the technique of vacuum cooling and plodding for manufacture of soaps. This technique will increase the Beta phase content

of such soaps and thus impart the requisite firmness and lathering quality to the soap even when using little quantity of Coconut Oil.

Development of fat-splitting industry

The need for cheap and good quality raw materials imposes the need for developing the fat-splitting industry which may be popularised along with distillation of fatty acids and their subsequent processing. This will enable the soap and glycerine industry to avail of the following advantages:

1. Fat splitting industry, if properly developed, will enable the effective utilisation of cheaper raw materials like Tallow, Acid Oil, Cottonseed Soap Stock, and low grade inedible oils and fats leading to the manufacture of a variety of fatty acids and their many derivatives which find application in soaps and other products like syndets, wetting agents, emulsifiers, synthetic rubber, printing inks, plastics, plasticisers, textile and leather-finishes, cosmetics, pharmaceuticals, etc.

2. These fatty acids when used in the manufacture of soaps will offer the following advantages:—

(*a*) Fatty acids offer a brighter soap without undesirable smell.

(*b*) The residual glycerine left in the soap will be negligible thereby rendering it less hygroscopic and therefore less amenable to sweating.

(*c*) Soap boiling operation will be simplified because neutralisation of fatty acids is more easy than saponification of oils while it also eliminates the need for subsequent brine washes, etc.

(*d*) For the above reason the loss of dissolved soap in spent lye and the formation of nigre in soap pan could be eliminated resulting in added economy to the process.

(*e*) For the same reason the consumption of steam in soap-manufacture could be reduced considerably.

(*f*) Neutralisation of fatty acid can be done by soda ash or caustic soda so that it offers the necessary flexibility to the soap-maker to avail of economic advantage whenever their prices fluctuate.

(*g*) The process of manufacture of soaps from fatty acids is more amenable to continuous operation and automation.

3. The sweet water obtained by fat splitting can be processed more advantageously than the soap-spent-lye for the following reasons:—

(*a*) Sweet water contains a higher concentration of glycerine with less impurities so that it consumes less steam for evaporation and less chemicals for treatment.

(*b*) For the above reason it facilitates increased utilisation of the installed capacity of the glycerine plants.

(*c*) The absence of salt in sweet water minimises corrosion possibilities with consequent increase in life of process-esquipment.

(*d*) For the same reason it eliminates the operation of extraction of salt from the evaporator.

(*e*) The absence of salt in sweet water also makes it more amenable to the ion exclusion process for manufacture of C. P. Glycerine.

4. The splitting process also increases the commercial yield of glycerine per ton of fat which is normally not attainable by the conventional soap boiling methods.

The above reasons provide ample justification for promoting the fat-splitting industry. The expediency with which this could be implemented will depend very much upon the true appreciation of the above advantages.

Modernisation of soap industry and the need to establish facilities for plant fabrication

We are living and working in an era of rapid technological developments so that the industry has to think in terms of modernising its outmoded equipments and practices in order to produce more and better products at cheaper cost. This need for modernisation is more imperative when the industry has to initiate its export trade against competition in foreign markets. Modernisation of the industry is further necessary to enable a planned expansion on sound lines particularly in the wake of the third plan period.

However, as we talk of modernisation of soap industry at a time when the country is short of foreign exchange even to pay for core of the present plan, it does become necessary to think in terms of working gradually towards self-sufficiency in the supply of these modern equipments, the moment the steel position improves. This, in no way, is easy to achieve, but then it has got to be tackled if the country's economy has to thrive and the industry has to flourish.

Thus it becomes necessary for the Government, the enterpreneur and the technician to pull their resources together and to plan and work out a comprehensive scheme for organising the designing and fabrication of process equipment in the country with necessary collaboration with foreign firms if available. In this connection, the profession of the consultant engineer has to be initiated so as to guide the industrialist in his ventures so that finally they may, as a team, face the challenging situation with the necessary co-operation from the Government.

In this context it is gratifying to note that a few firms have already made a beginning in this direction. It is hoped that they will be encouraged to launch further ventures, so that such co-ordinated efforts of the Government, the Industry and the Profession may finally lead towards realising well-organised facilities for designing and fabrication of plants to meet the requirements of oil, soap, glycerine, paint and allied industries even as pointed out by Sir J. C. Ghosh of the Planning Commission sometime ago.

Conclusion

Under the context of the various problems facing the industry it is gratifying to note that the Section for Oil Based Industries in the Development Wing of the Ministry of Commerce and Industries, is doing valuable

work to promote the interests of the industry on rational lines. It is hoped that the newly constituted Development Council for Soaps will ably guide them in formulating realistic policies regarding the systematic development of the Soap and Allied Industry.

It is equally encouraging to note that the Research Laboratories and Educational Institutions at various centres in the country are constantly working towards solving the many technological problems of the industry.

Further, it is as very heartening to note that symposium on varied topics of interest to the oil and oil-based industries are being organised from time to time offering a common platform to all those interested in the industry to meet and exchange the benefit of their knowledge and experience.

Under the circumstance, the industry may well look forward with faith in its future to work in close collaboration with the Government on the one hand and with Research Laboratories on the other, so as to solve the many problems of its development and thus serve the vast consuming public who form our nation.

COTTONSEED OIL INDUSTRY IN INDIA

by N. Bhowmik

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Although India is one of the oldest cotton producing countries of the world, cottonseed industry has not yet been fully developed here on modern and scientific basis. Whereas in most important cotton producing countries like U.S.A. where 90 per cent of the cottonseed produced is crushed and the oil is utilized for edible purposes, in the manufacture of margarine, shortening and other food industries, here in India only 8 to 8.5 per cent of the total annual production (1.65 million tons) is used in crushing. The importance of cotonseed crushing industry in India will be apparent when it is realized that it is capable of contributing to the nation's wealth to the extent of over 10 crores annually. Cottonssed crushing will augment the oil resources of the country without increase in acreage under oilseed cultivation, lead to better utilization of the idle capacity of the crushing units, increase in employment opportunities ; provide scope for earning foreign exchange by export of cottonseed products and releasing more of costlier groundnut oil for export and develop self-sufficiency in regard to linter pulp or chemical cotton which is the basis of important industries like cellulose acetate for rayon; plastic and photographic film; nitro cellulose for leather cloth; celluloid high tenacity tyre cord viscose; explosives and lacquers; carboxy methyl cellulose; filler for crushing powders; etc.

2. The growth of this industry in India has been rather slow on account of various reasons:

(i) Age-old custom of the Indian farmer to feed his cattle with whole cottonseed instead of cottonseed cake, with the mistaken belief that the latter is less nutritious, has led to a large demand of cottonseeds as fodder. This factor coupled with speculative trading has pushed up prices of seed beyond crushing parity and hindered the the progress of the industry.

(ii) The whole seed cannot also be directly crushed in village *ghanis*.

(iii) The oil content of the seed is small compared to other seeds like groundnut, etc. The yield is also reduced if crushing is done without delinting and hulling operations.

(iv) There is also the difficulty in disposing of the hulls and linters.

(v) The colour of the oil is very dark and is almost inedible without special refining.

(vi) The difficulty in disposing the soap stock or foots resulting in the process of refining.

3. *History*: A general interest in the possibilities of the cottonseed oil industry in India was first evinced in 1907 followed by establishment of a model cottonseed mill by the Government in 1908 at Kanpur. M/s. Indian

Cotton Oil Co., Navasari (1909) are mentioned as pioneers in the production of cottonseed oil. Subsequently, in 1938 a complete plant for delinting and hulling cottonseed was installed by M/s. Mody Industries Ltd., Modinagar, which unfortunately had to be sold to a South African firm only after a few months of working, owing to the dull marketing conditions prevailing at that period (1939). Subsequently several experts and committees from 1944 onwards had advocated the development of this industry pointing specifically to the wide scope of this industry in India, if proper scientific procedures were adopted.

4. *Plan Target*: The Planning Commission in 1951 fixed a production target of 12,500 tons of cottonseed oil. The Commission fully realized the difficulties in the way of rapid development of this industry in the country. In the Second Plan period, 1956-61, a production target of 30,000 tons of cottonseed oil has been fixed. The Development Wing of the Ministry of Commerce & Industry expect that the industry will produce nearly double the quantity laid in the Plan target. An *ad hoc* committee on cottonseed has been formed who is looking into the problems connected with this industry.

5. Production of cottonseeds in India is related to the production of cotton. The Planning Commission has fixed a target of production for raw cotton at 6·5 million bales in the Second Five-Year Plan. This would yield at least 1·85 million tons of cottonseeds.

6. *Distribution of Cotton and Cottonseeds*: Relevant data regarding production of cotton and cottonseeds in India is given in Table No. I. Out of the total production of 1·65 million tons of cottonseeds, nearly 35 per cent is of the American variety and the balance 65 per cent is of *Deshi* type. Production of American type of cottonseed is mainly concentrated in Punjab, Bombay, Mysore and Madras. This seed is preferred by millers who do delinting and hulling.

7. In general the oil content of the American varieties of cottonseeds in India is higher than that of Deshi seed. In this connection, it may be mentioned that several Deshi varieties of seed, e.g. Kakinada's, Mongari's (Andhra State); Nadam and Uppam (Madras State); Virnar and Pratap (Bombay State); Caorani (ex-Hyderabad State); Jarillas (Madhya Pradesh); Deshi seed in Punjab; Doddahatti (Mysore); and Buris (Ahmedabad) contain 18 per cent and higher oil on 10 per cent moisture basis. Thus not only American seed but also selected Deshi seed can be processed economically.

8. The Technological Laboratory of the Inidan Central Oilseeds Committee have also compared the oil present in different varieties of cottonseeds produced in the country. They have observed that the oil content in Indian cottonseeds varies from 12 to 22 per cent on 10 per cent moisture basis. Hirsutum varieties which give long-staple lint have higher percentage of oil. The Aboreum seeds on the whole give less percentage of oil, whereas, Herbaceum seeds are intermediate between the two in this respect. The Barbadense seeds also give high percentage of oil. Reports of the Regional

Research Laboratory at Hyderabad and the Central Food Technological Research Institute, Mysore, are given in Table No. II.

9. Ginneries in India are the sources of supply of cottonseeds for commerce, and as such, the regional distribution of ginneries are of importance from the standpoint of cottonseed industry. It may be mentioned in this connection that the ginning industry in India is of seasonal character. The season follows closely the harvest of cotton and varies in different regions as follows:—

September to April in Punjab, Madras and U.P.

October to June in Madhya Pradesh, Bombay and Khandesh.

November to April in Gujrat.

Many of the ginneries are situated in the black cotton soil tracts of Bombay, Madhya Pradesh, Madras and Mysore. The regional distribution of ginneries in India is given below:—

States	No. of cotton ginning factories.	No. of cotton pressing factories.
Andhra Prdaesh ...	24**	39
Assam ...	4	7
Bihar ...	—	—
Bombay ...	1278**	567*
Kerala ...	—	—
Madhya Pradesh ...	140	88
Madras ...	146	22
Mysore ...	471	91
Orissa ...	—	—
Punjab ...	(a)	134
Rajasthan ...	127	56
Uttar Pradesh ...	12	14
West Bengal	9	6
Delhi ...	—	—
Himachal Pradesh ...	—	—
Tripura ...	2	2
	2213	1026

* Includes 8 factories in Bombay which press cotton waste and repressed cotton.

** Excludes factories in former Hyderabad State for which list is not available.

(a) Not available.

10. *State-wise location and capacity of cottonseed oil mills.* The following statement shows the number of organized cotton oil mills in different States. Their installed capacity (in terms of seed) and also state-wise availability of seed:—

Serial No.	Name of the State.	Present availability of cottonseeds (in(tons)			Annual installed capacity of cottonseed oil mills in the organized sector (in tons)		
		Desi	American Type	Total	Already installed.	Licensed under the Ind. (Dev. & Reg.) Act, but not installed.	Total
1.	Andhra Pradesh	20,000	27,000	47,000	19,000 (2 units)	19,000 (1 unit)	38,000 (3 units)
2.	Madras	75,000	50,000	125,000	25,000 (1 unit)	—	25,000 (1 unit)
3.	Mysore	50,000	75,000	125,000	39,000 (2 units)	12,000 (1 unit)	51,000 (3 units)
4.	Bombay	662,000	100,000	762,000	110,000 (7 units)	173,400 (7 units)	283,400 (14 units)
5.	Madhya Pradesh	179,000	50,000	229,000	45,000 (1 unit)	24,000 (1 unit)	69,000 (2 units)
6.	Rajasthan	39,000	19,000	58,000	Nil	Nil	Nil
7.	Uttar Pradesh	16,000	—	16,000	Nil	Nil	Nil
8.	Delhi	—	—	—	Nil	Nil	Nil
9.	(including PEPSU)	50,000	230,000	280,000	161,600 *(in the unorganised sector)	Nil	161,600 (in the unorganized sector)
10.	West Bengal	—	—	—	Nil	Nil	Nil
11.	Bihar	—	—	—	Nil	Nil	Nil
12.	Others	11,000	—	11,000	Nil	Nil	Nil
		1102,000	551,000	1653,000	238,000 (13 units) organized)	228,400 (10 units)	628,000 (466,400 in 23 organized units and 161,600 in unorganized sector.)

* Not equipped with delinting and hulling machnes.

The annual installed capacity of units in the organized sector as shown in the above statement is in relation to experller capacity. Some of the units do not possess sufficient capacity for delinting and hulling to match their production. It is necessary that the organized sector should balance their plants by adding sufficient capacity for delinting and hulling.

11. *State-wise Production*: The present production of cotton seed oil in the different States both in the organized and unorganized sectors for the year 1957 is given below:—

Sr. No.	Name of the State	Production in the organized sector (tons)	Production in the unorganised sector (tons)	Total (tons)
1.	Andhra Pradesh	800	—	800
2.	Mysore	1605	—	1605
3.	Bombay	4874	—	4874
4.	Madhya Pradesh	1361	—	1361
5.	Punjab	—	6000	6000
		8640	6000	14640

12. *Consumption of cottonseed oil*: According to the information collected, consumption of cottonseed oil for different purposes has been as follows:—

(*i*) Estimated annual consumption in cooking	...	1000 tons
(*ii*) Utilization in the manufacture of vanaspati:	...	3940 „
(*iii*) Utilization in the produtcion of soap:	...	4000 „
Total	...	8943 „

13. *Export of cottonseed oil*: Cottonseed oil is being allowed to be exported at present free of export duty. Duty is not also levied on exports of decorticated and undecorticated cake. Exports of both are permitted freely. The export figures are given below:—

Year	Cottonseed oil Quantity (tons)	Value (Rs.)
1954-55	3193	39,70,520
1955-56	5428	65,61,050
1956-57	7648	120,00,381
1957 (Jan-Dec.)	8017	170,16,999
hydrogenated	121	1,84,022

14. The price of cottonseed oil is an important factor governing the entire economics of the cottonseed industry. For its development it should be competitive with that of groundnut oil in order to make it attractive for use in the vanaspati and soap industries to replace groundnut oil at least to some extent. The comparative prices of cottonseed oil and cottonseed cake with that of gronudnut oil during recent years are given in Table No. III.

15. *Problems of the industry*: The main problems confronting the the development of this industry are (i) creating a market for the oil; (ii) disposal of the cotton linters; (iii) disposal of the cake; and (iv) disposal of soap stock.

(i) *Creating a market for oil.* Crude cottonseed oil is very dark and cannot be used for edible purposes directly without refining. This fact has so far retarded the development of the market for cottonseed oil as cooking oil. The refining of cottonseed oil is to be undertaken immediately after

crushing, otherwise, it fixes the colour and the oil cannot be bleached effectively however drastic bleaching operation is done on it. A large number of mills do not possess their own refining plants attached to the crushing units. Besides, due to lack of sufficient technical knowledge about the refining of cottonseed (which is a highly technical process), the refining loss incurred is comparatively very high thereby makes the price of cottonseed oil not encouraging for use in different industries. It is claimed that use of continuous refining plant lowers the refining loss.

Provided the colour of the oil thus produced comes to an acceptable standard it is expected that about 43,300 tons of cottonseed oil may be consumed by vanaspati industry alone. (Target at the end of Second Plan is 4 lac tons. The Vanaspati Manufacturers' Association has already voluntarily agreed to add cottonseed oil to the extent of 2½ per cent in 1958, 5 per cent in 1959, 7½ per cent in 1960 and 10 per cent in 1961 in the production requiring 4,33,000 tons of vegetable oils). At least another 20,000 tons of this oil may be utilized by the soap industry at the end of 1961 (whose target of production is about 3 lac tons). Thus the disposal of 60,000 tons of cottonseed oil present no serious problem with the adoption of economic refining process for this oil.

(ii) *Utilization of cotton linters*: Another problem confronted by the industry is the disposal of cotton linters for which demand by the consuming industry has yet to be built up. At present there is no sufficient market for this production and the only way of its disposal is export. The Government have already agreed to abolish export duty on cotton linters in order to encourage export.

Cotton linters are the short fibrous material adhering to cottonseed after ginning and are removed from the seed by delinting machines. The linter content of the American variety of seeds is higher than that of the Deshi seeds. However, as already explained, in some varieties of Deshi seeds also the linter content is high and compares favourably with that found in American varieties.

In India there is hardly any demand for first cut linters on account of the relative abundance of cotton mill waste which is superior in many respects to linters for non-chemical uses. Prior to 1954 there was no consumption of linters in chemical industry. The present annual production of linters in India is of order of 1000 tons. At present the acetate rayon industry is able to utilize 1000 tons of indigenous second cut linters. The standard of linters needs improvement for being utilized in other industries. The progress made in the development of cellulose industry in the country gives a further opportunity for the development of cotton linter industry.

Below is given a list of principal manufactures for which the cotton linters will serve as raw material:

1. Cellulose acetate for rayon.
2. Acetate flakes for plastics moulding powder.

3. Triacetate for photographic film.
4. Nitro-cellulose for leather cloth, celluloid and explosives.
5. Low viscosity nitro-cellulose for lacquers.
6. Carboxy methyl cellulose.
7. Filler for ureaformaldehyde plastic moulding powder.
8. High tenacity tyre and yarn.
9. Viscose continuous filament yarn.
10. Staple fibre.
11. Transparent viscose film.

The requirements of linters for cellulose acetate, nitre cellulose, carboxymethyl cellulose, urea plastics filler and high tenacity tyre cord may be almost 6000 tons. In the manufacture of viscose continuous filament and staple fibre generally wood pulp is preferred. Though the suitability of linter pulp to replace wood pulp still remains to be investigated, it may be possible to substitute 20 to 25 per cent of wood pulp by linter pulp. This way. the last three items are capable of consuming another 14,000 tons. Thus the cellulose industry if properly developed during the next few years will offer a market for 20000 tons of second out linters after proper refining and bleaching. As against a production of 20000 tons of second cut linters about 10000 tons of first cut linters will be produced. A suitable market for disposing this 10000 tons of first cut linters could be found out. Due to its severe competition with the mill waste it cannot be profitably marketed in this country, and as such, it should be exported. With the recent abolition of export duty on linters such markets would easily be developed for export of 10000 tons of first cut linters. The amount of foreign exchange earned by exporting 10000 tons of first cut linter at an approximate value of Rs. 400/- per ton is around Rs. 40,00,000/- per year. In addition, the saving on account of indigenous linter pulp after the machinery have been imported will be nearabout Rs. 120 lacs per year.

(iii) *Disposal of Cake and Hulls.* Cottonseed hulls are produced while decorticating cottonseeds. Though it is being used in U.S.A. primarily as feed for livestock, it confronts a difficulty for disposal in this country. The meal provides protein concentrate whereas hulls serve the purpose of roughage in the feed. A number of crushing mills in U.S.A. market a mixture of decorticated cottonseed meal and hulls. Considerable quantities of hulls were also used during the War period in U.S.A. in the manufacture of furfural activated carbon, etc. It is understood that disposal of hulls in India by cottonseed oil mills equipped with delinting machinery does not present a problem so much as it is faced in creating a market for decorticated cottonseed cake as a cattle feed. Hulls are sold @ Rs. 1/8/- to Rs. 2/- per maund and used for cattle feeding purposes. M/s. Sundatta Foods and Fibres Ltd., Hubli, utilize hulls in the manufacture of composite pellets.

Cottonseed Cake. The present production of cottonseed cake in India both decorticated and undecorticated is of the order of 90,000 tons. The following quantities of cake have been exported during the last few years:—

Year	Quantity	Value
1954-55	1,117 tons	Rs. 2,30,761/-
1955-56	24,760 ,,	,, 68,41,971/-
1956-57	10,070 ,,	,, 32,42,082/-
1957 (Jan.-Dec.)	7,225 ,,	,, 22,43,335/-

The market in India for decorticated cottonseed cake is somewhat limited as the whole seed is preferred to the cake as cattle feed. The advantage of feeding cottonseed cake to cattle instead of whole seed has become accepted and the necessity for change is being appreciated by the farmers at present. As the price of cottonseed is generally determined by the price the farmers are ready to pay, sometimes the crushers do not have any parity for crushing. The price of cakes should also be competitive with those from other seeds. It is observed that the farmers who have been using whole cottonseeds for feeding their cattle do not like to use decorticated cakes. They would rather prefer using undecorticated cakes. The equivalent product can be made by mixing the hulls in the decorticated cakes. It is necessary that the following steps may be taken in order to encourage the use of cottonseed cake for cattle feeding purposes:—

(a) Manufacture of balanced ration for cattle feeding purposes consisting of decorticated cottonseed cake, hulls, rice bran, salt ,etc. should be encouraged.

(b) Intensive propaganda should be done through different organizations for popularizing cottonseed cake and for discouraging the use of whole seed as cattle feed.

(iv) *Utilization of cottonseed soap stock for industrial purposes*:—It has already been pointed out that raw cottonseed oil cannot be used for any purpose unless it is refined. It also shows much higher refining ratio as compared to other oils. Soap stock obtained during refining is an inevitable byproduct in the production of washed cottonseed oil. Due to its very dark colour it creates a problem for its disposal. Though some of the manufacturers of cheap quality soap use it to some extent, the material produced is not readily marketable and fetches low price. Cottonseed soap stock contains about 30 to 45 per cent of total fatty matter comprising of neutral oils ranging from 8 to 20 per cent. On the basis of refining of about 60,000 tons of cottonseed oil about 5,000 to 6,000 tons of fatty matter in the form of soap stock will be available per year. It is felt that the only possible way to dispose this huge quantity of soap stock is to convert it into a mixture of fatty acids of light colour by high temperature high vacuum distillation which serves as a better raw material in the soap industry. Utilization of these fatty acids in soap industry will release some groundnut oil for export. It should be possible to dispose the resultant pitch for road surfacing. The mixed fatty acids obtained by distillation may also find a market for rubber industry in the manufacture of greases, textile auxiliaries and synthetic detergents.

Appendix No. I

Production of cotton and cottonseeds in India.

States (as reconstituted)	Production of cotton (in thousand bales of 392 lbs. each)			Production of cottonseeds (in thousand tons)		
	1954-55	1955-56	1956-57	1954-55	1955-56	1956-57
Andhra Pradesh ...	158	131	135	55	46	47
Assam ...	8	9	9	3	3	3
Bihar ...	1	2	1	(b)	1	(b)
Bombay ...	2226	1921	2176	779	672	762
Kerala ...	8	10	10	3	4	4
Madhya Pradesh ...	433	403	653	152	141	229
Madras ...	256	335	358	90	117	125
Mysore ...	353	363	358	123	127	125
Orissa ...	2	2	2	1	1	1
Punjab ...	613	605	800	215	212	280
Rajasthan ...	126	184	167	44	64	58
Uttar Pradesh ...	34	29	46	12	10	16
Tripura ...	9	7	8	3	2	3
	4227	4001	4723	1479	1400	1653

(b) Less than 500 tons.

N.B. The proportion of cottonseed to cotton lint in Kapas (seed cotton) is 2 : 1 on an average.

Appendix No. II

Oil present in different varieties of cottonseeds processed in India.

Variety	Place of origin	Oil content (on whole seed basis) per cent
R.R.L. Hyderabad		
(Deshi)		
1. Gaorani 6	Nanded (Hyderabad)	18·0
2. R. K. 19	Raichur	15·2
3. Jawant	Koppal	16·7
4. Ca 12 F. 2	Latur	17·7
5. Jayadhar	Hubli	17·2
(American)		
1. Parbhani	Adilabad	16·4
2. Laxmi	Hubli	18·3
Central Food Technological Research Institute, Mysore.		
1. Laxmi (Gadag)		19·40
2. Indore No. 2	Indore	18·95
3. C. 520	Sahar	16·50
4. Kalyan	Virgaon	18·30
5. *Vijay*	Broach	15·15
6. *Navapar* (W. Khandesh)		13·95
7. Nander		17·40
8. Malvi No. 7	Indore	15·50
9. Jalgaon	East Khandesh	17·20

Appendix No. III

Comparative prices of cottonseed oil, cottonseed cake and groundnut oil (Rs. per maund).

Month ending	Cottonseed oil		Cottonseed cake		Groundnut Oil			
	Khanna	Bombay	Bombay	(Undecorticated) Khanna	Bombay	Madras (Expeller)	Kanpur (F.A.Q.)	Hyderabad
1	2	3	4	5	6	7	8	9
1955								
January	—	—	—	—	31·62	32·12	34·00	—
February	—	—	—	—	34·87	33·56	34·00	—
March	—	—	—	—	33·06	31·75	33·50	30·00
April	—	—	—	—	33·81	31·62	30·00	30·44
May	34·50	—	—	—	33·06	32·25	32·00	32·94
June	38·50	—	—	—	35·25	32·94	35·00	35·62
July	39·50	—	—	—	38·94	34·06	42·00	35·81
August	37·00	—	—	—	33·25	33·75	38·00	37·31
September	37·00	41·12	6·19	—	33·06	35·62	40·00	33·75
October	39·00	40·25	9·69	—	36·25	34·06	37·00	35·00
November	37·00	40·12	9·50	—	37·12	35·62	42·00	42·50
December	45·25	42·00	6·12	—	42·50	39·19	46·00	40·81
1956								
January	43·25	44·25	7·50	7·50	44·75	43·12	47·00	43·31
February	43·00	45·50	7·31	7·50	46·25	42·94	49·00	43·25
March	51·00	62·06	7·50	8·75	55·06	51·50	50·00	55·00
April	51·50		7·00	8·31	54·00	51·00	70·00	56·00
May	N.Q.	61·62	7·50	8·50	54·62	52·81	64·00	56·50
June	53·00	54·25	6·87	8·94	53·62	50·69	51·00	52·00
July	N.Q.	50·62	7·12	8·75	52·50	50·56	59·00	51·50
August	59·00	51·37	8·44	9·00	53·62	54·31	63·50	56·00
September	48·00	49·94	8·25	8·62	54·00	48·69	53·87	50·81
October	45·50	48·75	8·25	8·25	54·25	49·56	63·50	50·75
November	N.R.	58·75	8·25	7·00	55·75	53·00	62·00	55·00
December	49·50	55·50	7·87	7·00	53·81	51·19	57·00	53·31
1957								
January	54·44	62·50	7·12	N.R.	55·87	53·81	58·00	55·44
February	N.R.	54·12	6·87	6·75	52·12	49·87	55·00	54·19
March	51·25	53·62	6·62	7·00	55·50	51·81	57·50	54·19
April	54·75	53·88	7·12	8·00	56·50	52·69	58·00	73·75
May	57·50	56·52	7·37	8·00	60·37	54·69	64·00	59·19
June	56·50	55·62	N.R.	8·00	59·87	54·12	65·75	59·50
July	56·50	58·75	7·75	8·31	60·25	54·31	65·00	62·94
August	N.Q.	53·62	8·50	8·25	53·62	48·06	68·75	55·00
September	51·50	51·87	7·31	8·87	54·37	52·83	61·50	50·75
October	52·00	53·62	7·94	10·50	55·44	54·12	63·75	50·00
November	50·00	53·75	8·44	8·75	55·44	49·56	63·75	51·69
December	49·00	53·25	7·37	7·75	52·87	48·87	56·00	49·00
1958								
January	48·00	55·85						

NEWER AND BETTER USES OF NON-EDIBLE OILS

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Khadi and Village Industries Commission, Bombay

The importance of any oil, whether considered as edible or non-edible lies in its property or properties available to be utilized. In the initial stages of the vegetable oil crushing industry many oilseeds remained out of purview, as, due to crude crushing methods inferior quality of oil was produced, which was eventually subject to rancidity. Combined with this fact certain resinous matters etc. brought out along with the oil, as well as absence of refining methods made it impossible to use certain oils for edible purposes. The recent introduction of solvent extraction process and the refining process has served as a boon to improve the economy of oil crushing industry by releasing a larger percentage of oil and improving the quality of oil.

This article refers to non-edible oilseeds from trees like Mohwa (Bassia latifolia), Pilu (Salvodora oleoides), Pisa (Actinodaphne hookeri), Undi (Callophyllum inophyllum), Maroti (Hydnocarpus wightiana), Neem (Azadirachta indica), Nahor (Mesua ferrea) which are very rich in some fatty acid/or the other. Pisa Oil is considered as the only oil in India which contains 96 p.c. of Lauric acid, i.e. it is a better substitute for coconut oil and palm kernel oil. The Chemistry Branch of the Forest Research Institute, Dehra Doon, which initiated the chemical research on this oilseed, have further pointed out in their report (1934-35) that in view of the fact that Sodium lauryl sulphate is coming into considerable prominence as a base for new detergents, Pisa fat and similarly constituted fats of the Litsaea spp (N.O. Lauracea) over 60 varities of which are known to be found all over the country, could serve as better raw material for the purpose than the coconut and palm-kernel oil (trilaurin content under 50 percent) employed at present. Pisa fat can also be utilized for manufacture of confectionaries and agarbatties. Similarly the Pilu oil has more lauric and myristic acids that are important for soap making than even in Palm oil and Coconut oil. The difficulties experienced in import of coconut oil can be lessened to a considerable extent if the oils of Pilu and Pisa are made available.

Howver, a pre-condition to the scope for this utilization is the way in which these oilseeds will be made available for their newer and better uses. Though the end uses and their efficacy are established facts, it has yet to be considered how these oils can be properly processed even from their collection stage so as to enable further utilization.

Fatty Acids.*	S. Oleoides	Coconut Oil.
Capric	—	0·2 — 2
Caprylic	4·4	2·0 — 9·5
Capric	1·5 to 6·7	4·5 — 10·7
Lauric	21·2 — 47·2	28·0 — 51·0
Myristic	28·0 — 52·9	17·5 — 22·0
Palmitic	18·9	4·3 — 12·0
Stearic	— —	0·8 — 5·0
Oleic	5·5 — 12·0	2·0 — 10·3
Linoleic	1·3	1·0

(*From Khakhan fat as substitute for coconut oil in soap making by Dr. J. S. Aggarwal, National Chemical Laboratory, Poona-8.)

The potentialities of these oilseeds have been proved to be very great by the forest surveys. It remains to tap these vast resources by convenient and practical methods. These problems are far greater and more practical rather than chemical analysis.

The Khadi & Village Industries Commission's Scheme viz. the Non-edible Oils & Soap Industry has engaged itself not only in harnessing these non-edible oils for soap-making but it is trying to find out other industries in which non-edible oils can substitute edible oil. The inadequacy of the edible oils and fats hardly needs any elaboration. However, this itself gives an impetus to find out better uses of non-edible oils.

In the industrial field non-edible oil, like Mohwa, can be used for production of glycerine and even confectionaries besides soap-making. Neem oil though consisting of very common fatty acids can be used for the textile and rubber processing industries. The refining process as evolved and patented by the Council of Scientific & Industrial Research proposes do not only supply good neem oil for soap making (which will reduce the tendency to yield bad coloured and bad odoured soap) but even make available the bitter constituents separated during the process for the Pharmaceutical Industry. Though not yet experimented, this very commonly available oil has been even brought to the edible stage as a hydrogenated fat.

Karanja oil in its sulphonated form is a good material for tanning of leather. Undi oil can be used as a good water proofing material.

The oleic acid and other saturated acids available in some of these non-edible oils have been found to be extremely useful in the manufacture of rubber, carbon-paper, typewriter-ink, cosmetics and toilet articles, according to the reports of work done at the Regional Research Laboratory, Hyderabad, for the separation of high purity oleic and saturated acids from tallow.

The uses of oils edible or non-edible have no difference when the required properties can be successfully separated. As such it does not add much by listing the number of uses each one has. The uses of oil in our country are yet indispensible though they are being replaced by synthetic products in developed countries. Our success lies, therefore, in taking cognizance of these non-edible oils, arranging for their proper supply to industry,

solving the technical problems, if any, in extraction of their oils and that too at an economic price.

The fact that our country is rich in these non-edible oil seed bearing trees is now generally accepted. What is needed is to assess the availability potentialities, without which it is not possible to draw up a clear-cut programme. The Khadi and Village Industries Commission has undertaken the task of exploiting these resources by organising agencies to effect collection of seeds during the season. If we mean to do the job properly, conditions for their adequate collection in time and their proper storage will have to be created locally, i.e. in the areas of their collections. These areas are the lakhs of villages scattered all over the country, which are usually cut off during the rainy season. Therefore, the necessity arises of tackling these problems at the village level and in conditions by making use of the talent available there. Mere academic discussions and laboratory work can be of little avail if we wish to fully exploit this source of wealth. All the science and technology required for the job will have to be made understandable at the village level and all tests will have to be measured and verified at the village laboratories. If the science and technology cannot be made to give results for the benefit of the layman at the village level, let it be understood, not even the most herculean efforts can crown out attempts with success. Hence, the necessity is to build an organisation for the purpose on a sound basis in order that the whole thing would become organised and take permanent roots. Once the seed-collector knows the technique of collection and storage, he will be assured of a proper wage and income. Therefore, our problem is how to get these raw materials in good condition, rather than how to use them.

The Khadi and Village Industries Commission has been engaged in this programme and a large number of centres say about 500 as on 31-3-58, have been started all over the country charged with the collection of these seeds and, of course, of pressing the oil from them and make use of them for making soap. At present they collect seeds sufficient only for their work, because of so many other problems, viz., lack of technical know-how, adequate funds etc. and market for the surplus oils may not be forthcoming. There need be no need to enter into a discussion of why these seeds are crushed by ghanis and not by the oil mills. Let us first tackle the basic problem, i.e. of effecting maximum collection of these seeds and then the other things will take care of themselves. What is not a problem, should not be made to distract us unnecessarily, lest we might miss the bus by our own mistakes.

Besides the Khadi and Village Industries Commission, the Indian Central Oilseeds Committee has also been talking about the development of this Non-edible Oil Industry. A number of research workers and Laboratories and State Governments have also evinced keen interest in this Industry in their own way. What is now needed is a proper co-ordination of activities by different agencies and a correct estimation of the technological development in all its aspects on the one hand and the requirements of the pattern of economy for raising the status of these non-edible oilseeds on the other.

Another vitally important point is that of fixing priorities of our programmes at the national level. We all realise the importance of the non-edible oil Industry. In the Second Five Year Plan, our Government has included this as a part of small scale and village industries under—"miscellaneous industries". Probably, at the time the Karve Committee went into the question it was not possible for any one to present adequate data for its consideration. Since then more information has become available. It is time that we all try to focus the attention of the Government to that this programme may be included as a major industry and given priority for development in the Third Five Year Plan.

SECTION B

APPLICATION OF EDIBLE AS WELL AS NON-EDIBLE OILS

UTILISATION OF COTTON SEED OIL IN VANASPATI MANUFACTURE

by P. N. Mathur

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Cotton seed having 13 to 22 per cent oil has been recognised as a valuable source of edible oil all over the word except India—where 1.7 million tons of cotton seed are produced annually but less than 6% is crushed for oil. The great part is consumed as a cattle feed.

Oils and allied products play a significant role in the Industrial Economy of any country. They contribute towards the improvement in the dietary and living of people create opportunity for employment, and enhance the Industrial wealth of the country. In other cotton growing countries like U.S.A. and Egypt efforts have persistently been made to develop cotton seed industry through Scientific and Engineering Researches with a view to introduce new processes, manufacture new products, and attain better working efficiencies.

There is absolutely no reason why India should not use its annual out put of about 1.7 million tons in order to increase the oil suuply by about 1.60,000 tons. Export of edible oil of this quantity would bring Re. 16 to 20 crores worth foreign exchange to the country and also help in solving employment problems.

Recently Govt. of India have shown an active interest for encouraging cotton seed crushing by abolishing excise duty on cotton seed oil and export duty on cotton seed cake and continuing a liberal export policy for these items. Cotton Seed Oil Committee has also been appointed by Government to recommend necessary steps for rapid development of cotton seed crushing and also to suggest ways and means so that the prices of cotton seed oil and its products can be brought and kept in parity.

Govt. of India have also asked Vanaspati Industry, which is the second largest food Industry in our country next only to the Sugar Industry, to use cotton seed oil in increasing proportions. Despite difficulties of obtaining good quality oil at present, the Vanaspati Industry has voluntarily undertaken to use cotton seed oil to the extent of 2½ per cent of their total oil requirements during 1958, 5 per cent in 1959 7½ per cent in 1960 and 10 per cent in 1961 as a contribution to the national endeavour in developing cotton seed crushing.

The production of Vanaspati in India during the year 1957 was 300,400 tons and the production is expected to go up to 400,000 tons by the end of second plan. There is a hope that 60,000 tons of cotton seed oil can be produced by 1960/61. This means if entire quantity of cotton seed oil is to be consumed by the Vanaspati Industry, the percentage of consumption would be nearly 15 per cent. This quantity can be consumed by the Industry for

the manufacture of Vanaspati as well as for the manufacture of hardened oil for industrial purposes provided the following conditions are fulfilled :—

(1) Oil of good bleachable quality is available for all Vanaspati Factories throughout India.

(2) Oil prices are reasonable. The price should be lower than G. N. Oil.

(3) Import licences for the entire quantity of foreign activated bleaching earth and Carbon which is needed for cotton seed oil, bleaching are granted to all factories.

Now it is the duty of the Oil chemists and Technologists to see how best they can use the maximum quantity of cotton seed oil in Vanaspati without effecting the quality of the finished products. As losses of oil and processing cost during the refining and hydrogenation vitally effect the industry, they should also try to reduce the losses to the minimum along with the processing cost.

Crude cotton seed oil is obtained in the Indian Market has a dirty deep dark reddish, black colour and disagreeable taste and odour. The F. F. A. usually averages from 1·5 to 4%.

Vanaspati factories usually like to use washed cotton seed oil instead of Crude Cotton Seed Oil. The Indian Standard Institute has fixed the following standard for colour and acid value of refined and washed cotton seed oil.

Characteristic	Requirement for— Refined oil	Washed oil
Colour in 1/4" cell on Lovibond scale expressed as Y + 10R ... not deeper than	10	30
Acid Value — (Max)	0·5	0·5

In our considered opinion these specification are not complete unless bleachability tests are also included. From our experience we find that often light coloured oils require more earth for bleaching than darker coloured oil. This is due to the pre-treatment of the oil. From Table No. 2 appended these observations can be verified.

For processing cotton seed oil several methods have been suggested and tested. Many processes are used from the age old simple treatment with caustic soda to the most modern refineries complete with high speed centrifuges and complex chemical treatment.

In India almost all factories are doing batch refining in Kettle hence the object of this paper is to deal with processing of washed cotton seed oil in these fatcories. Huge quantity of washed cotton seed oil has been treated by us with much success. Much work has been done in the Laboratory and plant for improving the quality and minimising the losses of oil as well as processing cost. The method found by us very successful is dealt in this paper.

Important points to be observed during Neutralising

1. Processing of the oil should be carried out independently of any other oil in initial stage.

2. Common Salt should never be used during neutralising as it is apt to fix the colour.

3. Temperature of oil during neutralisation should not be allowed to go beyond 60°C.

4. Soap stock should not be mixed with groundnut soap stock but it should be processed independently.

Processing of washed cotton seed oil for the manufacture of Vanaspati maybe divided in the following heads :—

1. Re: Refining and Washing
2. Bleaching
3. Hydrogenation including hydrobleaching.
4. Post neutralising and bleaching.
5. Deodorising.

1. Re. Refining and Washing:

The object of refining is to reduce maximum quantity of colouring matter by caustic treatment with the minimum refining losses. The following method gives very good result.

The oil is pumped in the Nentralisor at the lowest temperature i.e. about 26° to 30°C. It is heated slowly to about 35°C and then caustic soda solution of 30°Be' corresponding to what will be necessary for neutralising an oil of 0.75 per cent F. F. A. is added as rapidly as possible and the speed of the vessel is then increased to about 60 R. P. M. Agitation at high speed is continued for about 15 to 20 minutes and oil is heated upto 55°C. Heating upto 60°C may go in exceptional cases. 0.1 per cent of soda ash on the weight of the oil treated is sprinkled over the oil and stirring continued for about 15 minutes then stirring is stopped. After this quickly about 5 per cent of hot water calculated on the weight of total oil is sprayed and oil is allowed to stand quietly for about 6 hours.

After soap is removed the hot water washes are continued until oil is free from soap.

2. Bleaching

The colour which is left after neutralising is removed by bleaching. This is achieved by employing absorbents such as activated earth and carbon.

Bleaching material account for about 60% of the total cost of the materials required in processing cotton seed oil. If a substantial economy can be made in breaching, it will have much effect on the cost of production.

The lesser amount of bleaching materials used in bleaching will effect economy also in the amount of oil lost through retention by the activated carbon and bleaching clay.

Our experience is that oil, which is required for the manufacture of Vanaspati, need not bleach much before hydrogenation as red and yellow

pigments of the carotenoid are bleached in the presence of about ·05 to 0·15 per cent of activated carbon during hydrogenation.

For bleaching cotton seed oil no indigenous activated earth or carbon was found suitable. Bleaching earths used by us were Fulmont 500 C, Tonsil Optimum and activated Carbon was Farnell (English).

Re-neutralised and washed oil was dehydrated in the bleacher under vacuum of 27″ to 28″ and then bleached by adding various amounts of earth and carbon to get the desired bleaching. It is always advisable to have the bleaching tests done in the Laboratory prior to plant bleaching. This gives the exact idea about the amount of earth and carbon to be taken during bleaching.

The oil after bleaching was filtered through the filter press. The residual oil from the filter press cake was removed by blowing fresh air and then passing steam. The oil recovered was dark in colour but it was taken back to the process. The press cake, even after air blowing and steaming treatment, contained about 20 to 30% oil.

For removing even this oil from the press cake, it was heated in open pans along with water and sufficient quantity of caustic soda solution was added to saponify the released oil from the cake. The soap made was black but it fetched fairly good price in the market. The recovery of oil reduced the losses further. Now only 1 to 2·5 per cent of oil is left in the press cake, which is ultimately rejected.

TABLE NO. 1

Losses during neutralising and bleaching of neutralised Cotton Seed Oil.

Serial No.	Quantity of oil in tons.	% F.F.A. of oil before neutralisation.	% F.F.A. of oil after neutralisation.	Oil after neutralising & bleaching in Tons	Loss of oil in tons	% Loss.
1.	32·92	0·25%	0·05%	32·23	0·69	2·1%
2.	33·17	0·22%	0·06%	32·47	0·70	2·1%
3.	33·88	0·16%	0·05%	33·24	0·64	1·9%
4.	32·84	0·12%	0·04%	32·25	0·59	1·9%
5.	32·10	0·09%	0·05%	31·55	0·55	1·7%
6.	16·60	0·19%	0·05%	16·28	0·32	1·9%

From the above table No. 1 it is quite clear that refining losses are quite low.

Properly refined and bleached cotton seed oil can be hydrogenated without any trouble. It has been observed that during hydrogenation certain changes occur in the fat apart from an increase of its melting point and a decrease of Iodine values.

One industrially important consequence of hydrogenated oil is that the hardened fat is decolorised. Carotenoid pigments are markedly bleached. This observation has led to the development of a technique for removing the

colour from an oil without essentially hardening it, though some reduction in Iodine values are hardly to be avoided. This technique is called hydro-bleaching. The table No. 2 appended shows the colour reading of processed oil at different stages.

3. *Hydrogenation including Hydrobleaching.*

For obtaining best results during hydrogenation the following process is recommended.

Refined and bleached oil is taken into converter and it is heated upto 110°C under vacuum. At this stage about 0·1% carbon is sucked into the converter. Hydrogen gas is circulated through the oil for about 1 hour at a pressure of about 15 Lbs. After this treatment is over about 0·1% nickel catalyst (Rufert or Resistol C) is taken inside the converter and temperature is raised to 130°C with stirring under vacuum. Heating is continued upto 160°C under hydrogen gas pressure.

After 160°C hydrogen gas is circulated inside the converter and pressure is maintained about 1 atmosphere. When the desired M. point is obtained the flow of hydrogen is cut off and charge is cooled down to temperature suitable for filtering out the catalyst.

Hydrogenated cotton seed oil with a M. point of 37°C or higher show extremely good keeping qualities.

4. *Post Neutralising and Bleaching.*

If the hydrogenation is not done properly often there is more increase in F. F. A. % of the hardened oil. In order to reduce the F. F. A., it is essential that hardened oil should again be neutralised, washed and bleacehed. But in case there is not much increase in F. F. A.% there is no point in neutralising the oil. The oil should simply be bleached by using only ·05 to 1% earth.

There is only negligible change in colour during post refining and bleaching. From table No. 2. this can be seen.

5. *Deodorising*:—

In order to remove the odour and taste from the hardened cotton seed oil, the oil is deodorised. Deodorising is done by treating the oil by steam at high temperature i.e. between 180° to 200°C under high vacuum. The time of deodorising in the case of cotton seed oil is more than Groundnut oil.

Deodorising Effects On Oil :—

(1) Deodorising removes odoriferous volatile constituents from the oil and makes it fit for edible purposes.

(2) Destroys carotenoid pigments in the oil and thus decolorise it. The colour drop is probably due to bleaching under heat—which is characteristic of cotton seed oil.

(3) Reduces the free fatty acid of the oil.

Table II

Serial No.	Washed Oil in ¼″ Cell. Y—R	Y+10R	Neutralised, Washed & Dehydrated Oil Y—R	Y+10R	Bleaching Materials Quality	% used.	Bleached oil. in ¼″ Cell Y—R	Y+10R	In 5¼″ Cell Y — R	Hydrobleached & Hydrogenated oil In 5¼″ Cell Y — R	Post Refined & Bleached Oil In 5¼″ Cell Y — R	Deodorised Oil In 5¼″ Cell Y — R
1.	23—2	43	14—1·2	26	Fulmount 500C	0·35	3·6—0·4	7·6	37·5—5·8	20·1—2·7	20·0—2·6	16·5—1·8
					Carbon							
					Farnell	0·15						
2.	22—1·5	37	12·2—1	22·2	Tonsil Optimum	1·0	4·0—0·6	10	39·0—7·5	26·0—2·7	22 —2·5	18·0—1·8
					Carbon							
					Farnell	0·25						
3.	19—1·8	37	11·5—1·10	22·5	Tonsil Optimum	0·5	4·9—0·5	9·9	38·0—6·0	23·0—2·80	22·0—2·5	17·0—1·7
					Carbon							
					Farnell	0·25						
4.	14—1·4	28	10·0—1·0	20	Tonsil Optimum	0·5	3·5—0·3	6·5	36·5—5·4	22·0—2·3	21·0—2·3	16·0—1·9
					Carbon							
					Farnell	0·25						
5.	16·0—1·4	30	10·0—1·1	21	Tonsil Optimum	0·6	4·0—0·3	7·0	37·0—5·6	22·5—2·6	20·6—2·5	16·0—1·9
					Carbon							
					Farnell	0·25						
6.	22·0—1·4	36	10·0—1·1	21	Tonsil Optimum	0·25	4·1—0·4	8·1	36·5—6·0	24·2—2·9	23·0—2·6	16·0—1·8
					Carbon							
					Farnell	0·25						

SURFACE-ACTIVE PROPERTIES OF SULPHATED ESTERS OF CASTOR OIL FATTY ACIDS

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Abstract

Sulphation of methyl, ethyl and butyl esters of castor oil fatty acids has been studied with a view to obtain products better than Turkey red oil. The sulphated esters were found to be incompletely miscible with water inspite of their appreciable contents of organically combined SO_3. When extracted with petroleum ether, the products gave raffinates which were found to be far superior to Turkey red oil in wettability, foaming, and stability to acids, alkalis and calcium salts.

Castor oil, on account of its cheapness in comparison to many fatty oils and its large content of ricinoleic acid (mono-hydroxy, mono-unsaturated), has ever been an attractive industrial raw material. The textile industry has been using it since a long time in the form of Turkey red oil.

Realising that the Turkey red oil as commonly produced lacks greatly in stability to acids, alkalis and hard water, many modifications have been suggested in its manufacturing technique—such as use of solvents during sulphation (Naik and Desai, 1948), use of lower or higher temperatures during sulphation (Stirton, 1954 ; Uppal, 1946-47), use of sulphating agents other than sulphuric acid (Naik and Desai, 1948 ; Stirton, 1954), etc. The products thus obtained were shown to have better performance compared to the Turkey red oil.

An alternative to the sulphation of castor oil is the sulphation of its fatty acids or other unsaturated fatty acids and their derivatives. Sulphated oleic and ricinoleic acids are stated to be more surface-active than the corresponding sulphated glycerides (Schwartz and Perry, 1949). Sulphated lower alkyl oleates and ricinoleates are said to be good rewetting and softening agents (McLeod, 1954 ; Miller, 1953 ; Schwartz and Perry, 1949). Sulphated amides are found to be stable at high temperatures in the presence of acid or alkali and resistant to hard water (Stirton, 1954). However, the extent of their improvement compared to Turkey red oil has not been known. Therefore, in the present work, the performance of the sulphated lower alkyl castor oil fatty acids esters as surface active agents has been investigated.

Experimental

I *Preparation of Methyl, Ethyl and Butyl Esters of Castor oil.*

The esters were prepared by two methods—one was the common method consisting of the successive operations of saponification of the oil, splitting of the soap and esterification of the resulting fatty acids ; the other was alcoholysis.

Purified anhydrous methyl and ethyl alochols and a fraction of B. P. grade butyl alcohol distilling between 116° and 118°C were used for esterification and alcoholysis. The latter reaction was catalysed by sodium methoxide.

The constants of the raw materials and the various esters finally obtained are given in Table I. Analysis was carried out according to the official A.O.C.S. methods.

TABLE I

Characteristics of Methyl, Ethyl and Butyl esters of Castor Oil fatty acids

Esters	Acid value	Sap. value	Iodine value (Wijs)	Hydroxyl value	Esterification %
Castor oil (raw)	2·3	181·2	82·4	164·6	—
Castor oil (refined)	0·1	181·0	82·2	164·8	—
Mixed fatty acids	179·8	191·4	87.2	—	—
‡Methyl esters	7·8	181·9	82·8	156·8	95·7
‡Ethyl esters	9·6	174·8	78·7	135·5	94·7
‡Butyl esters	9·9	166·5	73·4	119·8	94.5
‡Methyl esters	0·4	181·0	82·1	164·6	99·9
‡Ethyl esters	0·4	175·1	79·3	158·2	96·4

‡Esters obtained by esterification.
‡ ,, ,, ,, alcoholysis.

II. *Sulphation of the Esters.*

Concentrated sulphuric acid, oleum (20 per cent) and chlorosulphonic acid were used as sulphating agents. At a time 100 g. of the esters was sulphated by adding a specific quantity of the agent, keeping the temperature of the mixture constant. Addition of the agent required 15 to 30 minutes and the mixture was stirred further for a definite time at the above constant temperature. The mixture was cooled to 20°C., mixed with a solution of 10 per cent sodium sulphate and allowed to separate for two hours. The lower acid layer was drawn off and the upper fatty layer was neutralised at 30°C to 7 *p*H with 20 per cent NaOH solution.

The following factors were varied to see their influence on the extent of sulphation as measured by the SO_3 contents of the products—proportion of the sulphating agent on weight per cent of the material to be sulphated ; time of reaction ; and temperature of sulphation.

The sulphated products obtained were analysed according to the official A.O.C.S. methods, except soap which was estimated by the method given by Burton and Byrne (1946).

The results are given in Tables II, III, IV and V. For comparison, analytical values of two commercial samples of Turkey red oils, one laboratory-prepared sample of Turkey red oil and one patented product, are given in Table VI.

TABLE II

Sulphation of Methyl, Ethyl and Butyl esters of Castor oil with Sulphuric acid (Temperature: 30°C).

Ester	Sulphuric acid %	Time of reaction hours	Sulphated Fatty Matter %	Water %	Acid value	Soap mg. equivalent of COONa in 10 g. of sample	SO_3 % (Anhy-F. M. basis)
	20	5	70·6	26·9	18·3	2·1	7·4
Methyl	30	4	67·5	28·6	20·3	2·9	9·0
Ester	40	3	68·1	27·3	24·6	1·9	10·2
	50	2	64·4	31·5	22·6	2·3	11·3
	20	5	68·7	28·1	21·3	1·7	7·3
Ethyl	30	4	66·3	29·8	24·1	1·9	9·2
Ester	40	3	64·8	31·1	22·6	2·3	10·4
	50	2	62·7	34·5	26·9	2·7	11·7
	30	4	69·9	27·3	23·7	2·4	6·8
Butyl	40	3	64·6	31·0	26·2	1·9	7·6
Ester	50	2	68·7	26·8	29·3	2·6	8·7

TABLE III

Sulphation of Methyl and Ethyl esters of Castor oil with Oleum. (Temperature : 30°)

Esters	Oleum %	Time of reaction hours	Desulphated Fatty Matter %	Acid value	Water %	SO_3 % (Anhydrous F.M. basis)
	30	3	65·0	26·3	21·1	10·3
Methyl	40	1	58·7	23·7	25·2	12·4
Esters	50	1	55·1	25·1	28·0	13·3
	30	3	68·7	21·9	17·8	9·9
Ethyl	40	1½	63.5	19·7	20·3	12·1
Esters	50	1	69·8	26·8	12·6	13·0

TABLE IV

Sulphation of Methyl esters of Castor oil with Chloro-sulphonic acid.
(Temperature: 30°C)

Chloro-sulphonic acid %	Time of reaction hours %	Desulphated fatty matter %	Water %	Acid value	SO_3 % (Anhydrous F.M. basis)
30	2	77·3	15·2	27·8	5·6
40	1½	47·0	39·9	16·9	9·7
50	1	68·2	19·8	29·2	8·5

TABLE V

Sulphation of Methyl esters of Castor oil with 30% Sulphuric acid at different temperatures.

Temperature of sulphation °C	Time of reaction hours	Sulphated fatty matter %	Water %	Acid value	SO_3 % (Anhydrous F.M. basis)
20	6	70·1	27·6	19·4	8·4
30	4	67·5	28·6	21·3	9·0
40	1½	65·3	31.7	24·6	9·6
50	¾	68·8	26·5	29·6	8·3
60	½	70·2	27·3	32·3	7·5

TABLE VI

Analysis of some Turkey red oils.

Sample No.	Sulphated fatty matter %	Water %	Acid value	Soap mg. equivalents of COONa in 10 g. sample	SO_3 % (Anhydrous F.M. basis)
1	64·5	31·9	36·7	2·6	9·6
2	78·6	19·7	48·8	5·6	6·1
3	72·1	24·9	38·6	6·9	7·2
‡4	41·9	54·6	9·3	...	14·1

III. *Solvent Extraction of the Sulphated Products.*

Commercial petroleum ether supplied by M/s. Burmah Shell Co., was used for extraction. This had a boiling range of 70° to 90°C.

50 ml. of the sulphated product was shaken with a definite quantity of the petroleum ether. The factors that were varied were the ratio of ether to the product and the number of extractions. One sample of Turkey red oil was also extracted with petroleum ether four times, using a ratio of three parts of petroleum ether for each part of the Turkey red oil by volume. After thorough agitation in a separating funnel, the mixture was allowed to separate for one hour. The lower layer (raffinate) was drawn out from the bottom of the separating funnel. The solvent-rich upper layer (extract) and the raffinate were freed from the solvent and analysed.

The monoglyceride contents of the Turkey red oil fractions were determined according to the method of Pohle *et al.* (1950).

The experimental values are given in Tables VII, VIII and IX.

TABLE VII

Analytical characteristics of the raffinates of sulphated Methyl, Ethyl and Butyl esters of Castor oil.

Expt. No.	Sample	No. of extractions	Ratio of sulphated product to ether (first extraction)	Raffinate %	Extract %	Desulphated Fatty Matter %	SO_3 % (Anhydrous F.M. basis)
1.	Sulphated Methyl esters of Castor oil	1	1 : 4	73·5	26·5	59·9	16·6
2.		1	1 : 10	67·0	33·0	56·3	18·7
3.		2‡	1 : 4	66·5	33·5	53·5	18·8
4.		3‡	1 : 4	64·5	35·5	51·4	22·1
5.		Original Sample	—	—	—	68·6	11·3
6.	Sulphated Ethyl esters of Castor oil	1	1 : 4	75·0	25·0	51·8	14·8
7.		1	1 : 8	72·6	27·4	48·7	17·5
8.		2‡	1 : 4	67·7	32·3	45·5	18·6
9.		3‡	1 : 4	65·2	34·8	43·2	21·2
10.		Original Sample	—	65·5 —	—	62·7	11·7
11.	Sulphated Butyl esters of Castor oil	1	1 : 6	79·2	20·8	62·5	12·7
12.		1	1 : 8	73·5	36·5	37·1	16·3
13.		2‡	1 : 4	66·5	33·5	54·3	18·4
14.		3‡	1 : 4	65·5	34·5	52·6	21·1
15.		Original Sample	—	—	—	68·7	8·7

‡ The 2nd and 3rd extractions were done with a ratio of solvent to product as 2 : 1.

TABLE VIII

Analytical characteristics of the extracts of sulphated Methyl, Ethyl and Butyl esters of Castor oil.

Sample	Fatty Matter %	Acid value	Sap. value	Iodine value (Wijs)	Hydroxyl value	SO_3 % (Anhydrous F.M. basis)
Unsulphated Methyl esters	99·0	48·1	190·2	58·6	68·6	0·07
Unsulphated Ethyl esters	98·1	41·3	188·2	58·5	67·3	0·08
Unsulphated Butyl esters	98·0	51·3	186·3	58·5	65·7	0·08

TABLE IX

Analytical characteristics of the Sulphated and Unsulphated portions of Tureky red oil.

		Yield by weight on anhydrous F.M. basis %	Fatty matter %	Acid value	Monoglycerides % (Anhydrous F.M. basis)	Soap mg. equivalent of COONa in 10 g. sample	Fatty acids % (as ricinoleic on anhydrous F.M. basis)	SO_3 % (Anhydrous F.M. basis)
1.	Original sample	—	64·5	36·7	35·8	4·3	28·3	9·6
2.	Unsulphated portion	22·4	99·1	125·0	26·3	0·3	66·4	0·03
3.	Sulphated portion	77·6	45·7	17·3	10·6	4·6	9·2	13·3

IV. *Evaluation of the Properties of the sulphated Products.*

The various products were tested for their 1. Wetting Power. 2. Acid Stability 3. Alkali Stability 4. Alkali Solubility and 5. Calcium Ion Stability by the methods described by Harris (1954). In addition, the 'foaming power' was measured by the height of the foam produced when 25 ml. of a 0·25 per cent solution of the product was shaken in a 100 ml. measuring cylinder. Values are given in Table X.

TABLE X

Surface-Active Properties of the Sulphated Products.

No.	Product	SO_3 content %	Wetting time seconds			Acid stability ml. H_2SO_4 (10%)	Calcium Ion stability ml. $CaCl_2$ (10%)	Foaming Power cms.	
1.	T.R.O. No. 1, Table IX ...	9·6	11	38	114	0·2	3·0	2·4	0·8
2.	T.R.O. raffinate No. 3, Table IX ...	13·3	8	31	109	0·5	3·0	2·9	·9
3.	Ether extracted sulphated Methyl esters Expt. No. 1, Table VII ...	16·6	5	18	60	16·0	7·0	5·6	2·4
4.	Ether extracted sulphated Methyl esters Expt. No 3, Table VII ...	18·8	4	11	55	18·0	7·0	6·8	2·7
5.	Ether extracted sulphated Methyl esters Expt. No. 4, Table VII ...	22·1	2	10	42	35·0	7·0	8·9	3·8
6.	Ether extracted sulphated Ethyl esters Expt. No. 9, Table VII ...	21·2	3	8	31	26·0	7·1	8·6	3·1
7.	Ether extracted sulphated Butyl esters Expt. No. 14, Table VII ...	21·1	11	32	112	20·0	7·0	8·0	2·8
8.	Calsolene oil HS ...	14·1	6	19	68	140·0	7·0	8·0	3·0

1. SO_3 contents of products Nos. 1, 2 and 3 are expressed on the sulphated fatty matter: those of the rest, on the desulphated fatty matter.
2. The three wetting times are given for 0·5%, 0·25% and 0·125% concentrations respectively of the products in water.
3. Products Nos. 1 and 2 were alkali-unstable and alkali-insoluble. The others were completely stable and soluble.
4. The two values under 'Foaming Power' refer to the heights of foams as measured immediately after shaking and after 5 minutes after shaking.

Discussion

The Esters—It is to be noted from Table I that alcoholysis gives better yields of the esters than esterification. Between the two types of esters, the former are marked by low acid values. Also they have hydroxyl values which do not very much differ from the theoretical. The low hydroxyl values of the latter esters are, no doubt, due to the formation of lactones and lactides. The proneness of ricinoleic acid to form lactones and lactides is also seen from the low acid value of castor oil fatty acids.

Sulphation :—SO_3 content which is a measure of sulphation increases with increase in the amount of the sulphating agent (20 to 50 per cent). However, with increase in the temperature of sulphation (20°C to 60°C), the SO_3 content increases to a value of 9·6 at 40°C and drops down.

In general, the SO_3 contents of the various sulphated esters lie in the following order (decreasing) :

Methyl and ethyl esters sulphated with oleum ;
Methyl and ethyl esters sulphated with sulphuric acid ;
Methyl esters sulphated with chlorosulphonic acid ;
Butyl esters sulphated with sulphuric acid ;
Commercial Turkey red oils.

Comparison of the compositions of the sulphated esters with those of Turkey red oils (Tables V & VI) shows that their total fatty matter contents, soap contents and acid values are fairly similar. The patented product —Calsolene Oil HS.—has the highest SO_3 content of all of them, while the sulphated esters on an average are found to have SO_3 contents of 3 to 4 units higher than the commercial Turkey red oils. The latter were completely miscible with water while it was surprising to note that the former gave turbid solutions. Even on warming, the turbidity did not disappear. This would be definitely considered a defect in practical application. Attempts to remove this defect led to the treatment of the sulphated esters with petroleum ether.

Solvent Extraction:—The first extraction of the sulphated esters with petroleum ether removed nearly 1/4th of its portion as unsulphated, leaving in the aqueous phase all the sulphated portion and a small quantity of the unsulphated portion. The first raffinate was completely miscible with water. Further extraction had the effect of increasing the SO_3 content of the raffinate until after three extractions, the SO_3 content was very near the theoretical. (Table VII)

It is seen that multiple extraction enabled almost complete separation of the sulphated from the unsulphated portion. The yields of the raffinates i.e. the active portions, were found to be about 65 per cent of the original sulphated products. It is also seen from Table VIII that the extracts are almost all fatty matter since all the water accompanies the sulphated portions which are not dissolved by the petroleum ether. The extracts are highly acidic (20-25 per cent acids) indicating hydrolysis of the products during sulphation and washing. Their low hydroxyl values indicate the

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formation of lactones and lactides while low iodine values indicate some reaction at the double bond during sulphation and washing. The SO_3 contents of the extracts are negligible.

Multiple extraction of one sample of Turkey red oil (Table IX) led to the removal of nearly 22 per cent of unsulphated matter (extract). Thereby the SO_3 content of the remaining portion rose up to 13·3 per cent. The theoretical SO_3 content of a completely sulphated (i.e. trisulphated) castor oil (based on sulphated fatty matter and taking hydroxy acid content of castor oil equal to 90 per cent) is 18·5 per cent. This shows that the degree of sulphation in the portion that was sulphated was as high as 72 per cent. It is, however, difficult to calculate the proportions of mono-, di- and tri-sulphated portions in this product.

It is to be noted that commercial Turkey red oils have lower SO_3 contents than the sample in Table IX (see Table VI). Therefore, the unsulphated portion in them must be greater than 22 per cent. Yet these Turkey red oils are completely soluble in water. On the other hand, the sulphated esters showed turbidity in water. The reason for this difference in the behaviour of the two products is likely to be in the solubilising effect of a large triglyceride molecule in the former product. The comparatively smaller ester molecules do not probably have this property.

Performance Tests:—Taking the wetting power, acid stability and other properties of Turkey red oil given in Table X as standard for comparison, the following conclusions are drawn :

1. Although solvent extraction of the Turkey red oil has increased its SO_3 content, the SO_3-enriched product has yet the same performance as the original product.

2. All the solvent extracted sulphated esters are found to be far superior to the Turkey red oil in every respect. Their acid stability is remarkably increased while they are alkali-stable and alkali-soluble.

3. The surface-active properties of the sulphated esters are enhanced with the number of extractions with concurrent increase in the SO_3 contents.

4. Between the esters themselves, the sulphated methyl and ethyl esters are a little better than the sulphated butyl esters.

5. The solvent extracted products compare very favourably with the patented product (Calsolene Oil HS) in all respects except the acid stability which the latter possesses in a remarkably high degree.

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PREPARATION AND UTILISATION OF DEHYDRATED CASTOR OIL (DCO)

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Dehydrated castor oil (DCO) is a drying oil manufactured from non-drying castor oil, by a process of dehydration and is considered to be intermediate in properties to linseed oil and tung oil.

A large number of both inorganic and organic catalysts have been employed for the dehydration of castor oil (Kaufmann and Ganeff, 1949). Among the inorganic catalysts sulphuric acid, sodium bisulphate, phosphoric acid, oxides of aluminium, tungsten, titanium, zirconium, molybdenum, uranium, thorium, lead, manganese, cobalt, zinc as well as their phosphates, sulphates and silicates, boric acid, silicic acid, oxides, sulphides or chlorides of phosphorus, arsenic, antimony, silicon, sulphur, selenium or tellurium, activated carbon, silica gel and infusorlial earth in amounts ranging from 0·1 to 3·0 per cent have been mentioned. Pyrosulphuric acid and persulphuric acid and their alkali metal salts have also been claimed as efficient catalysts for this purpose. Among the organic catalysts, sulphonic acids, mono- and di-butyl and cresyl phosphoric acids. toluyl sulphochloride, halogenosulpho acids, brominated and inorganic salts of certain fatty acids, polybasic organic acids such as phthalic, adipic or maleic acids have been used. Dole and Keskar (1053), Saraf and Dole (1957*a*, 1957*b*) investigated the activity of a large number of sulphonic acids towards the dehydration of castor oil and found toluene sulphonic acid as useful dehydrating catalyst at 280°C. Phenol sulphonic acid gave paler products than benzene sulphonic acids. Phosphoric acid afforded exceptionally pale-coloured dehydrated product with low acid value.

Osnos and Golovistikov (1940) compared various catalysts and found sulphuric acid especially efficient. Forbes and Neville (1940) obtained highly unsaturated dehydrated castor oil samples by using clay, sodium bisulphate, phosphoric acid and the anhydride of tungstic acid as catalysts. The amount of water liberated served as a measure of the effectiveness of the catalysts.

Work carried out at the Regional Research Laboratory, Hyderabad, on the dehydration of castor oil (DCO)

India is one of the biggest producers of castor oil. Castor oil is a major agricultural product in Andhra Pradesh, the production being almost half of India's total production of this seed. The utilisation of castor oil in various ways to produce semi-finished and finished materials has, therefore, been of great interest to the Regional Research Laboratory, Hyderabad. Work has been carried out on dehydration of castor oil and on the use of dehydrated oil in varnishes and alkyd resins. For the dehydration of castor oil our process is based on the use of sodium bisulphate as a catalyst. When

this catalyst is used by itself, the dehyrdated oil obtained is dark in colour, has high acid value and the film formed after drying continues to show tackiness. It has been found that the addition of sodium bisulphite (0·4 per cent) with sodium bisulphate (2 per cent) to the castor oil at 180-200°C reduces the colour of the final product. A preliminary treatment of raw castor oil with activated carbon and fuller's earth improves the quality of the dehydrated castor oil. The dehydration of the oil may be carried out at 220-240°C under high vacuum. The bubbling of carbondioxide or any other inert gas under these conditions is unnecessary. It has been further found that if a weak alkali like slaked lime (2 per cent) is added immediately after dehydration before cooling, the acid value of the oil is reduced and the dehydrated oil gives a fairly non-tacky film on drying (Sivasamban *et al.*, 1952).

The other and still more recent advance has been the discovery that dehydrated castor oil itself can be made free from after-tack by suitable alterations in the mode of manufacture.

This new type of DCO is known as monomeric DCO and one of its special features which distinguishes it from the ordinary DCO is its low viscosity. The process by which the monomeric DCO is produced in western countries is a closely guarded secret. By the use of catalysts like sodium bisulphate and sulphuric acid, dehydrated castor oil of a viscosity less than 2·5-3·0 poises at 25°C is not obtained, whereas the theoretical viscosity of monomeric dehydrated castor oil in which all the molecules are in the monomeric state is 1·2 poises. It has been found that the addition of 0·4 to 0·8% of zinc dust or sodium sulphite on the weight of the oil along with sodium bisulphate at 220-240°C prevents polymerisation of the dehydrated castor oil during the process and lowers the viscosity of the final product (Sivasamban *et al.*, 1956).

Pilot plant experiments on the preparation of various grades of dehydrated castor oil have been successfully carried out using Kestner's isoelectric synthetic resin plant. This consists of a reaction vessel with motor driven stirrer connected through an air condenser and water condenser to a receiver through which it is connected to a vacuum pump. Heating is by mineral oil in a jacket surrounding the reaction vessel by means of electric immersion heaters with thermostatic control. 20 lb. batches of castor oil were processed in this plant. The general procedure followed is to heat the refined castor oil to 220-240°C under vacuum of about 28 inches of mercury. When this temperature is reached a slurry of catalysts, sodium bisulphate etc. in a small amount of castor oil is added without breaking the vacuum. After allowing sufficient time (½ to 1 hour) for the dehydration of the oil, slaked lime in the form of slurry prepared from DCO from the previous charge is added, stirring continued at 220-240°C for about 10 minutes and the charge rapidly cooled under vacuum. For bodying up to 25·0 poises a further time upto 4¾ hours is required and for bodying upto 36·2 poises 5½ hours is needed; the bodying temperature being 280°C.

The insoluble material is removed from the cooled dehydrated product by centrifuge. The entire process is completed within 5-6 hours.

The Regional Research Laboratory, Hyderabad, is now in a position to offer processes for the manufacture of the following grades of dehydrated castor oil:

1.	Quality O	... Ordinary DCO
2.	Quality M	... Monomeric DCO
3.	Quality B	... Bodied DCO
4.	Quality BB	... Highly bodied DCO

The various characteristics of these four grades of DCO are given in Table I. The Indian Standards and A.S.T.M. Specifications for the various grades of DCO are also given for the sake of comparison from which it may be seen that except for slightly more colour the monomeric dehydrated castor oil (Quality M) compared very favourably with the A.S.T.M. specifications for unbodied DCO. The Quality B satisfies the Indian Standards Specification in all respects. Quality BB also compares with the A.S.T.M. specifications for bodied DCO. The costs of monomeric and bodied DCO have been found to be only 0·17 and 0·34 rupees per pound more than the price of the refined castor oil.

Oleoresinous varnishes from DCO

Medium oil length varnishes have been prepared from ordinary and monomeric DCO with ester gum and were examined for colour, drying time, water and alkali resistance. Similar products were prepared from boded linseed oil (25 poises) and their characteristics were also determined for the sake of comparison.

The results show that the use of DCO in varnishes makes them superior to those based on linseed oil; varnishes based on monomeric DCO are in their turn superior to those prepared from ordinary DCO. The following observations are of interest in this connection:—

(1) Monomeric DCO is found to be more reactive than ordinary DCO in varnish production and a slight addition of a stronger thinner like xylol or butanol to white spirit in their formulations has been found useful.

(2) Varnishes based on DCO are superior in drying time and alkali resistance to those based on linseed oil; the alkali resistance of the varnish based on DCO especially of monomeric quality improves on ageing.

(3) The slight aftertack found in varnishes from ordinary DCO is completely absent in those based on monomeric DCO.

Alkyd resins from DCO

The use of castor oil, bodied and momomeric dehydrated castor oil in the preparation of oil modified alkyds has been studied. Short, medium and long oil alkyds have been prepared from these oils by the monoglyceride method using xylol as the azeotropic solvent.

The castor oil alkyds are light coloured and give substantially non-tacky films on air drying and hard and glossy films on stoving. Short oil DCO -glycerol alkyds give heavy wrinkle finishes on heating at 120°C. In the case of long oil alkyds the use of monomeric DCO enables the production of

alkyds giving completely tack free films on drying. Alkyds of higher viscosities and lower acid values can be obtained by the use of monomeric DCO without any risk of gelation.

Conclusions

DCO, as far as we are aware, is not being manufactured in India so far on a large scale. A few factories appear to be manufacturing it on a small scale for their own use but the samples examined by us were dark in colour and not conforming to any standard specifications. The results of our work, briefly summarised in this paper show that the use of dehydrated castor oil in varnishes and alkyds is of definite advantage, this advantage is emphasised if the monomeric grade of DCO is used. India is one of the biggest producers of castor oil in the world. It is also much cheaper than tung oil, which has to be imported and is in short supply at present. The conversion of raw castor oil to monomeric dehydrated castor oil is a comparatively easy and cheap process. It is gratifying to note that a firm in Bombay has recently taken the process for its preparation.

Further work to improve the quality of the monomeric dehydrated castor oil by various treatments and investigations of its employment in various surface coatings are in progress at the Regional Research Laboratory, Hyderabad.

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TABLE I.
Characteristics of Various grades of DCO

	Various grades of DCO prepared at R.R.L.				Specifications		
	Quality O (ordinary DCO).	Quality M (monomeric DCO).	Quality B (bodied DCO).	Quality BB (highly bodied DCO)	IS : 81-1957	ASTM for unbodied DCO	ASTM for bodied DCO
Specific gravity, 30/30°C	0·9219	0·9322	0·9493	0·9515	0·944-·951	0·930-0·941 15/15°C	0·950-0·970 15/15°C
Viscosity, 30°C (poises)	2·5	1·65	22·7-27	slightly more than 46·8	15-25	1·4-2·5 (25°C)	36·2-63·4 (25°C)
Acid number	5·2	4·0	10·0	12·8	Max. 18	Max. 6	Max. 6
Iodine No. (Wijs 1 hr)	134·6	135·0	104·5	106·8	90-112	130-145	Min. 100
Colour (Lov. 1 cm.) Y	16·8	3·6	3·1	3·8	22	3	3·0
R	4·0	1·1	0·7	0·8	1·9 (calculated)	0·5	0·6
Refractive Index (25°C)	1·4807	1·4860	1·4860	1·4861	—	1·4805-1·4825	1·4860-1·4885

VEGETABLE DRYING OILS—THEIR ROLE IN NAVAL PROTECTIVE COATINGS

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The role of drying oils in the field of coatings has been discussed with special reference to naval protective coatings. The impact of modern developments in the synthetic resin field on the utilisation of drying oils in protective coatings has been indicated. In this country, producing a large tonnage of drying oils, it is natural that protective coating formulations should incorporate drying oils in a large measure. Anti-corrosive paints for protection of ships' hulls against submerged corrosion, antifouling paints, which prevent settlement of biological fouling organisms on submerged hulls, and weather-work primers and finishing paints, which protect superstructures of ships from marine atmospheric corrosion, are the most important classes of naval protectives. The problems associated with the incorporation of drying oils in the formulation of these coatings are discussed in detail against the background of marine corrosion and fouling. The facilities available for testing and the research and development projects undertaken by the Naval Chemical and Metallurgical Laboratory, Bombay, in the field of naval protective coatings are briefly indicated.

This paper deals with the specific role of drying oils in naval protective coatings. Present day requirements in the protective coatings field are extremely diverse and in many cases highly exacting. To meet these requirements, fast-drying synthetic resin based lacquers, emulsion paints, and hot applied plastic coatings, have been introduced in recent years and have reduced dependence on drying oils. However, the use of drying oils as such or in modified form, still continues in protective primers, where flexibility and adhesion are major considerations. Drying oils with polar fatty acid groups have much better adhesion, particularly to ferrous surfaces. In the absence of polar groups, modern synthetic resins like vinyls, present serious problems of metallic adhesion, necessitating elaborate surface preparation of substrates. In the absence of adequate adhesion even the most protective film would fail due to flaking of the coating. Specially formulated 'wash-primers' based on reactive resins like polyvinyl butyral have been designed for improving adhesion of vinyl based coatings. (Steel Structurals Painting Council specification, U.S.A. 1953). Use of synthetic resins alone usually involves use of greater quantities of solvents than are necessary with drying oils to produce materials of paintable consistency. Because of this, drying oil-based coatings can produce comparatively thicker films than is possible with synthetic resin coatings of comparable consistency. This is a very important consideration in the protective field. Lesser number of coats would be required to produce optimum thickness when drying oil-based coatings are used. Jordan (1955) has indicated that paint films suffer an average loss of one mil (0·001″) per year due to deterioration and has, therefore, stressed the need for high initial thickness. For protection against atmospheric corrosion a thickness of 5 mils is considered essential and for protection of ships' hulls against corrosion and fouling, at-least 7 mils thickness is required.

Drying oil films alone does not have sufficient resistance to abrasion, permeability to moisture and atmospheric degradation, hence the need for

incorporation of suitable synthetic resins and pigments to produce effective coatings as demanded by modern requirements in protection. The incorporation of various resins and pigments would naturally depend on the environment in which the coatings are likely to be used. The marine environment is one such typical environment and protective problems associated are discussed here in detail. For those interested in paints and protective coatings, Lawrence and Gale (1947) regard a ship as an "easily corrodible mass of metal half-submerged in a highly corrosive liquid medium"—the sea. The main problems associated with such an environment are atmospheric and submerged corrosion and marine biological fouling. Large quantities of weather-work paints to protect the superstructure and anticorrosive and antifouling paints for protection of submerged hulls are consequently used.

Marine Corrosion

The corrosion rate of structural steel in sea water and atmospheric corrosion rate in marine atmosphere have been determined by various workers (Hudson 1940 ; Ambler and Bain 1955 ; Forgeson *et at,* 1958). The submerged corrosion rate is in the region of 4-6 mils an year and does not differ substantially in temperate and tropical waters. Atmospheric corrosion rate of steel depends on the humidity, pollution and temperature at the site. In tropical marine regions it varies from 3-4 mils a year. In this country, preliminary work on atmospheric corrosion rates is being carried out by the Technical Development Establishment Laboratory, Kanpur (now Defence Research Laboratory, Stores) (1956) and immersed corrosion rates in sea water by the Naval Chemical and Metallurgical Laboratory (NCML) Bombay, at various sites. All ferrous structures exposed to or submerged in marine environment need adequate protection from corrosion. To prevent a metal from corroding, it must be denied its supply of oxygen and water, as the corrosion reaction, which is electrochemical in nature, cannot proceed in their absence. Unfortunately enough water and oxygen would diffuse through most organic protective coatings than that required for normal corrosion rate of uncoated steel (Mayne, 1952). Thus it is impossible to arrest corrosion by organic barriers alone. The cathodic reaction responsible for corrosion cannot be inhibited by the most impermeable of films. In protection against submerged corrosion in sea water, organic protective films should have very low ionic permeability and high alkali resistance (alkali being released from cathodic areas). Unfortunately the resistance to ionic permeability of straight drying oil films is very poor. Phenolic and alkyd varnishes are superior in this respect and vinyl resin films have the highest resistance. This has been demonstrated by Kittleberger and Elm (1952), who have found that ionic diffusion is directly related to the electrical resistance of the films. Recently, Mayne and Maitland (1957) have shown that straight linseed oil films have poor electrical resistance due to their water sensitivity and the pattern of distribution of the moisture retained in the film. There is low resistance between the cathodic and anodic areas of

the substrate due to such films, which would, therefore, be unable to prevent corrosion. Alkali resistance of these films is also very poor, the alkali released from cathodic areas and the alkaline pH of sea-water (8·2) tends to saponify and soften glyceride and ester linkages. Consequently straight linseed oil or alkyd and epoxy esters of linseed fatty acids do not offer protection under submerged conditions in sea water. Phenolic-linseed stand oil varnishes have superior alkali resistance and low ionic permeability. However, due to the ingress of moisture and oxygen, corrosion of substrates does take place even under such resistant films and therefore the need for inhibitive pigmentation. There are three classes of inhibitive pigments:—

1. Basic soap-forming pigments like red lead, basic lead sulphate, basic lead carbonate and zinc oxide.
2. Soluble pigments like zinc chromate and zinc tetroxychromate which passivate steel surfaces.
3. Metallic anodic pigments like zinc dust which protect ferrous surfaces by galvanic action.

In addition, there are barrier pigments like aluminium powder and iron oxide which increase the resistance to moisture permeability.

The most effective inhibitive pigmentation of linseed and resin modified linseed oil films is by soap-forming pigments. Mayne and Van Rooyen (1954) have shown that the degradation products of lead linolenate and linoleate (linseed oil fatty acids) like lead pelargonate, suberate and azeleate, inhibit corrosion of iron and steel even at pH as low as 4·2. The exact mechanism of inhibition has not yet been established; but it is believed that these soaps function by adsorption on the metallic surfaces. Recently developed lead cynamide and calcium plumbate have also been shown to behave in a similar fashion in straight linseed oil media (Read, 1950).

Effective under-water anticorrosive ship-bottom compositions have been developed by the British Iron & Steel Research Association, based on rosin modified phenolic resin in linseed stand oil and incorporating basic lead sulphate, basic lead carbonate, zinc oxide and iron oxide as inhibitive pigments. (Fancutt and Hudson, 1947). An improved composition based on a partial replacement of linseed stand oil by tung oil in the medium and replacement of basic carbonate lead by aluminium powder in the pigments has also been developed by the same authorities. These are now being used extensively by ships.

Red lead in linseed oil was found to give superior protection to structural steel in an industrial atmosphere at Sheffield for 13 years and a marine atmosphere at Calshot for 17 years in atmospheric exposure tests on protective painting of steel made by the British Iron and Steel Research Association (Fancutt and Hudson, 1957). Subsequent tests have confirmed the superiority of primer formulations based on linseed oil incorporating inhibitive pigments like red lead, basic lead sulphate and zinc chromate over media incorporating synthetic resins like alkyd, cumarone and phenolic. Linseed oil paint films are generally more elastic than those of other paints and are, therefore, able to adapt themselves without rupture or flaking on

even imperfectly prepared substrates. Synthetic resin based paints, however, exhibit improved performance after adequate surface preparation. Alkyd-based zinc chromate primers belong to this class.

The resistance to weathering i.e. deterioration by condensed moisture, heat, ultra violet and oxygen, of linseed oil films is not very satisfactory. This leads to "yellowing" and, due to polymer degradation "chalking" of pigmented films, which affects adversely the appearance and cleanliness of finishing paints based on linseed oil alone. They have been replaced completely by alkyd-based synthetic paints, incorporating rutile titanium dioxide, zinc oxide and antimony oxide (incorporated for its fire-retardance) in Naval weather-work paints. Modern fatty-acids Epoxy-ester-based weather-work paints have yet to show superiority over alkyds in performance and economy. Their adhesion to metallic surfaces is reported to be better than alkyds; but weather-work paints are seldom used without a priming coat of red lead in linseed oil or zinc chromate in alkyd medium.

The temperature sensitivity and flexibility of tar and bitumen paints can be improved substantially by incorporation of drying oils and pigments like aluminium powder forming useful and economical protective coatings, where appearance is not a primary consideration (Fancutt and Hudson, 1957).

Marine Fouling

The settlement of marine organisms on submerged portions of the hull constitutes a serious problem. Settlement usually occurs under static conditions, when organisms are in the free swimming stages. Once settled, they continue to grow unless dislodged by the ship's velocity when she is moving. Most fouling larvae are unable to settle, if the rate of water movement is greater than 2 knots, so that ships lying in harbour collect most fouling organisms in slack water, and not when the tide is running strongly. Unless properly controlled, the problem assumes serious proportions and affects the ships' operational efficiency adversely. Fouling causes an increase in resistance to movement of the hull due to increase in the friction coefficient of the hull and in extreme cases of fouling the increased dead load is likely to reduce speed and increase fuel consumption to maintain original speeds. An indirect effect of fouling results in ships being dry-docked periodically for removal of fouling and renewal of under-water coatings. This naturally increases the cost of dry docking as well as the cost due to operational loss of the ships while in dry dock. The effect of fouling on speed and fuel consumption is generally more serious on Naval Ships than on Merchant Ships. The former, particularly in peace time, spend long periods at anchor, conditions more conducive to settlement of marine fouling, while merchant ships usually work on a regular routine with static periods reduced to a minimum. Consequently Naval ships require more effective protection against fouling than that required by Merchant ships. Other troublesome effects of marine fouling are found in the fouling of pipes and conduits conveying sea-water in ships and shore establishments resulting in blocking of the pipes and sometimes corrosion by sulphate-reducing

bacteria. In addition, marine borers attack wooden structures like piers, jetties and wooden hulls. If allowed to function unhampered, they would virtually destroy entire structures.

Before any work on antifouling measures are undertaken, it is necessary to determine the nature, extent and seasonal variation in the attachment of different groups of fouling organisms with respect to any location. Studies of marine fouling organisms in Bombay harbour have been carried out and similar studies at Cochin and Vizag and other Indian harbours is also being initiated. Heavy fouling has been observed in Bombay harbour during summer months and negligible fouling during monsoon by Ranga Iyengar, Gopalakrishnan and Kelkar (1957). Biological activity is related to salinity and temperature at the site. During the monsoon salinity drops significantly due to dilution by rain water water and nutrients are affected adversely causing decreased incidence of fouling. Barnacles, Bryozoans, Hydroids and Tube-worms are the most important fouling organisms, Barnacles being the worst offenders as they burrow into soft paint films causing severe damage. Wood boring organisms tolerating low salinity conditions like Sphaeroma and Martesia have been observed in damaged wood from Cochin waters by Gopalakrishnan (1957).

Numerous antifouling measures have been investigated from time to time. Of the physical methods, use of ultra-sonics to prevent fouling has been found to be too expensive. Radio-active, beta emitter, Thallium 204 has also been tried for prevention of fouling but the dosage required for satisfactory antifouling effect was found to be high enough to be uncomfortable to human being (Morely *et al.*, 1958). Protection obtained by antifouling paints has been the most economical and effective so far. These paints usually incorporate toxic compounds of copper and mercury in an organic binder, formulated in such a manner that on immersion, the toxins are released in the sea water at a steady rate. This builds up repellant/lethal concentrations of the toxin in close proximity of immersed panels. There are two types of antifouling paints differing in the release of toxins from the paint. The soluble matrix type, where the binder is dissolved by saponification by the alkaline sea-water, thus exposing fresh surfaces of the toxin to sea water. The other is the insoluble matrix type, where toxic release is achieved by erosion of the medium and by continuous contact of toxic particles obtained by the highest possible loading. The cold-applied soluble matrix type antifouling paints form the largest group used on commercial vessels. They are inexpensive, easy to apply and afford adequate anti-fouling protection for about an year (the normal preiod between dockings) and have good storage life. The vehicle of these paints is usually based on acidic resins like rosin and shellac. Any paint resulting from these resins would also be acidic and tend to dissolve to some extent in the mildly alkaline sea water. Rosin used alone, however, results in a very brittle film having poor flexibility and its solubility in sea water is also very high. To overcome these short-comings, plasticizers, restrainers and toughеners have to be incorporated. Oleoresinous materials like phenolic-linseed stand oil, blown

linseed oil, tricresyl phosphate and chlorinated rubber are some of the materials introduced in this class of formulation. This results in the solution rate of the vehicle being controlled and enables a steady and effective release of toxins. Drying oils thus assist in film formation, improving flexibility and helping in reducing the solution rate of rosin. Cuprous oxide and copper powder are the most common antifouling toxins. Mercuric oxide has also been used and is very effective; but due to hazards involved in painting with such paints it is being replaced entirely by copper compounds. Recently copper sulphide, copper thiocyanate and cupric hydroxide have shown some promise as toxins. Some organic toxins, natural and synthetic have also been investigated for antifouling purposes (Harris, 1952). Their toxicity appears to be specific for some particular fouling types.

Cold-applied insoluble matrix type antifouling paints are usually based on highly resistant media like para-substituted phenolic-linseed stand oil and tung oil or on wholly synthetic media like vinyl resins or semi synthetic media like chlorinated rubber. Here the toxic loading is of a very high order (90 per cent on non-volatiles) and resultant paints are very effective for almost double the period as compared to soluble matrix types; but are comparatively expensive. They have shown superior performance in conjunction with cathodic protection, where the alkali released from the cathodes saponifies most oleoresinous media. Other antifouling paints are of the hot application type. They do not incorporate solvents. They have been adopted mainly by the U.S. Navy and have not found favour in other countries. They usually produce very thick films and have been reported to have very good antifouling performance.

The rate at which poisons are released from the antifouling paint is an important consideration. This is termed as leaching rate. It should not be too high, as this would deplete the toxic content rapidly leading to early failure, nor too low, so that toxic concentration is inadequate, thus permitting fouling. It has been found by Ketchum *et al.*, (1945) in U.S.A. and Barnes (1948) in U. K. that irrespective of the type of the formulation, all effective antifouling paints should have a steady leaching rate of at least 10 micrograms copper per square cm. per day. The figure mercury is much lower and is in the region of 2 micrograms.

The testing of under water paints involves Laboratory examination for composition, raft evaluation of performance and ultimate assessment in ships trials. These are now being carried out by this Laboratory.

Research and Development on Naval Protectives at NCML

The following is an account of the various research and development problems in the field of Naval protective coatings being carried out by this Laboratory:—

A raft has been moored off Bombay Harbour providing for the first time within the country, facilities for sea-water assessment of anticorrosive and antifouling compositions, timbers against marine borer attack and metals for resistance to submerged corrosion and fouling. Paint exposures have been

commenced in 1954 and data regarding raft life of currently available commercial underwater compositions has been obtained. Most successful anticorrosive compositions do not have a life of more than 35-40 weeks on the raft ; while the best antifouling paints have not lasted more than 25-30 weeks. Best soluble matrix type oleoresinous antifouling compositions have given a maximum raft life of about 2 years in temperate waters in U. K. With currently available indigenous materials, it would, therefore, be desirable to formulate antifouling paints having raft life of at least 1 year in tropical waters, where fouling and temperature are much more severe. Anticorrosive paints should have a raft life of at least 18 months.

In view of comparatively lower raft life of commercial under-water compositions, it was decided to investigate on improved experimental antifouling and anticorrosive compositions with a special emphasis on utilisation of indigenously available drying oils and natural resins like shellac. The Indian Lac Research Institute, Namkum, carried out some work on shellac-based under-water compositions and some of their experimental compositions were exposed on the raft in Bombay. Anticorrosive shellac-based formulations had a life of about 20 weeks. Antifouling paints based on similar media did not, however, last more than 6-10 weeks. Work was, therefore, carried out in this Laboratory for formulating improved shellac paints. An experimental shellac-based antifouling formulation incorporating copper powder as toxin was developed and it has shown satisfactory performance for 25 weeks on the raft. Three other types of antifouling formulations have also been prepared and exposed on raft. One of them is based on linseed stand oil modified phenolic resin and incorporates cuprous oxide as toxin. The second one is based on chlorinated diphenyl incorporating cupric hydroxide as the toxin and the third is based on chlorinated rubber incorporating copper powder as the toxin. They have unfouled surfaces for nearly 40 weeks. The last named formulation has also given excellent protection against Teredo borer attack on wood specimens. Some experimental anticorrosive compositions from the National Chemical Laboratory, Poona, have also been exposed on the raft.

Data on salinity, temperature, pH and seasonal variation of the settlement of fouling organisms are being regularly obtained in Bombay and Cochin harbours and have been published.

Biological studies on and Laboratory rearing of fouling larvae has just been started. These larvae have to be killed/repelled during their free-swimming stage before they settle on substrates. Biological testing of various indigenous organic natural toxins against fouling larvae is also being investigated.

Testing of underwater compositions pass through distinct stages depending on whether they are anticorrosive or antifouling paints. In the case of both these paints, it is necessary to carry out an initial chemical examination for composition. This is important to ensure that material tendered by commercial sources conforms to a definite composition so that certain repro-

ducibility is assured during performance. However, composition alone does not guarantee adequate performance, which must be assessed separately. Anticorrosive paints are subjected to Laboratory performance tests involving immersion in sea water and exposure to salt spray. In case of antifouling paints, no satisfactory laboratory performance test, which could correlate with actual antifouling performance, has yet been evolved. Some attempts to leach out both toxin and matrix in an accelerated test using sodium glycinate solutions have been carried out in U.S.A. Though successful in eliminating imperfectly formulated compositions, this method has not been able to differentiate between two good paints. Some investigations on modifying this method are under study at NCML. The present performance test of antifouling paints involves exposure for prolonged periods on the raft for antifouling assessment and leaching rate tests, which are carried out to find the maximum period a paint can maintain a steady leaching rate sufficient to prevent fouling. This is a long and time-consuming procedure. Any accelerated test to correlate with antifouling performance and steady leaching period would simplify testing these paints. Some work on accelerated testing of anticorrosive primers using the 'Highspeed Rotor Apparatus' has been carried out by the Chemical Research Laboratory at Teddington. It is proposed to have similar equipment in this Laboratory.

Wormwell and Brasher and several other workers like Mayne, Greenblatt etc. have carried out interesting work on the mechanism of break-down of paint and varnish films using electrochemical procedures. Some work on these lines has also been started in this Laboratory.

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SECTION C

SCOPE FOR NEWER AND BETTER UTILIZATION OF NON-EDIBLE OILS

INVESTIGATION OF LESS-KNOWN OILS IN HYDROGENATION INDUSTRIES: USE OF TOBACCO SEED OIL

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Abstract

For sometime past newer sources materials are being sought for replacing older and conventional source materials in the hydrogenation and other industries. In the present work, tobacco seed oil has been investigated as to its suitability for hydrogenattion for being used in edible fat and other industries. It has been estimated that a large quantity of tobacco seed oil can be available as a by-product by suitable modification of harvesting procedures and according to an official estimate about 3000 tons of oils were available for marketing in 1956-57. In the present work, investigation has been undertaken to find out the refining and hydrogenation characteristics of tobacco seed oil. Technical details such as nature and quantity of refining agents required, percentage loss in refining have been established. Further, the variation of the characteristics and chemical composition of the hydrogenated product, and condition of hydrogenation have been investigated. Points as to selectively, iso-acid formation, catalyst concentration etc. have been recorded.

Introduction

In the investigation of less known oil seeds and oils, tobacco seed oil was chosen first, since it was readily available at a comparatively low cost (Rs. 46·00 per maund) and characteristics of seed oil was well known from the previous work done in this laboratory (S. R. Chakrabarty and M. M. Chakrabarty, 1957). Since the central idea of this investigation is to find out the suitability of his seed oil as a newer source material for Vanaspati Industry, it was found advisable to study the selectivity of hydrogenation reaction and iso oleic acid formation which is very important for this partially hydrogenated edible fat. Selectivity in a general sense can be defined as the preferential reduction of more unsaturated molecule in fatty oil. Complete selectivity has never been achieved. In practice the condition established for the hydrogenation allow certain reactions to proceed at a faster rate than others and in this way provide some selectivity. The overall rate at which hydrogenation take place and the composition and characteristics of the final product depend upon the following facors: (i) the type of catalyst used, (ii) the catalyst concentration in the oil, (iii) the hydrogen gas pressure, (iv) the temperature of the reaction, and (v) the degree of hydrogen gas dispersion. The most important factor is perhaps the type of catalyst used. In this investigation, some trial runs with different catalysts e.g. catalyst supplied by M/s. Hindusthan Levers, by M/s. Swaika Vanaspati Products and Nickel catalyst made by wet-reduction process in this laboratory, rufert catalyst were tried. Amongst them, rufert catalyst was found to be best as regards its uniformity of behaviour and selectivity performances. Accordingly, this rufert catalyst was used in subsequent investigation.

Experimental

Tobacco seed oil (I.V. 139·6, F.F.A. content 1·47 per cent) was heavily coloured, the colour index determined by the Lovibond tintometer (B.D.H. pattern) through 1/4″ cell was as follows :

R : 0·6
Y : 8·8

As it was found inadvisable to take up this highly coloured oil direct for hydrogenation, studies on the refining characteristics of the seed-oil was taken up as sufficient data on that was not available. For this, alkali solution of different strength with different excess amount was applied for alkali refining and Fuller's Earth (B.D.H.), Bentonite, active charcoal and Fullmonth earth 511C (I.C.I.) was applied in different concentration in a series of experiments and colours of each samples were viewed through Lovibond tintometer. From the point of view per cent colour removal and per cent loss in refining, addition of 16° Be' alkali+0·25 per cent excess and 2 per cent Fullmont earth 511C+0·5 per cent carbon was found to be the most suitable condition. This condition was then utilised in the pilot refining equipment (De Laval oil refining unit). Total loss through alkali refining and vacuum bleaching (22″ Hg. 1 hr. treatment) was 18·5 per cent. This high loss could easily be remedied by taking a larger charge.

Degree of colour removal was quite satisfactory :

Red : 75%
Yellow : 71·4%

Coming to the hydrogenation—experiment proper, it was planned to carry out hydrogenation in a laboratory scale first to study the conditions and then to simulate this condition in the pilot-plant dead-end circulating type of hydrogenator that we possess. Accordingly, about 100 gms. of refined oil was charged in a three necked flask fitted with a magnetic stirrer. The oil was hydrogenated at temperatures ranging from 150°—180°C and at atmospheric pressure. In order to ascertain a better understanding of the hydrogenation reaction, the oil was hydrogenated to its maximum possible extent. 2 per cent Rufert catalyst (Nickel content 23·11 per cent) was used for this experiment. A series of samples at regular intervals were drawn and subjected to analysis. Report of the analysis are communicated below. Duplicability of the reaction conditions was tested with a larger amount of charge (1500 gm.). Analytical data of different samples collected from this batch are also reported. Cis-Linoleic acid was estimated by ultra violet spectrophotometric method and iso-oleic acid was estimated by the method of Cocks, Christian and Harding (1931).

Experiment I

Results:

Charge : 100 gms.
Catalyst : 0·5 % (active Nickel)
Temp. : 150°—180°C
Pressure : Atmospheric
Stirring : Medium. (from Magnetic Stirrer.)

TABLE 1.

Sample No.	Time of hydrogenation in hours.	I.V. of Oil (Wij's ½ hr.)	R.I. at 40°C.	Slip-point °C	Wiley M.P. °C
0 (Refined oil)	0	139·6	1·4690	—	—
1	1	128·0	1·4690	24	—
2	2	97·9	1·4665	32	—
3	3½	56·4	1·4615	48	53
4	4½	34·08	1·4595	56·5	62·5
5	5½	16·9	1·4571	63·0	68·5
6	6½	7·75	1·4550	66·0	71·5

TABLE 2.

Fatty acid composition

Sample No.	% Linolenic	% Linoleic	% Oleic (Total)	% Iso-Oleic	% Saturated (by difference)
0	1·6	71·5	12·2	1·1	14·7
1	—	60·0	23·5	11·9	16·5
2	—	25·2	57·5	23·84	17·3
3	—	0·6	64·1	37·24	35·3
4	—	0·3	38·7	21·04	61·0
5	—	0·2	18·6	8·25	81·2
6	—	0·1	6·5	3·20	93·4

EXPERIMENT II

Charge : 1500 gms.
Catalyst : 0·5% (active Nickel)
Temp. : 160°—165°C.
Pressure : Atmospheric
Stirring : Medium (from Magnetic Stirrer).

TABLE 3.

Sample new No.	Time of hydro-generation in hour.	I.V. of Oil (Wij's ½ hr.)	R.I. at 40°C.	Slip-point 0°C.
0 (Refined oil)	0	139·60	1·4690	—
1	2	118·70	1·4690	—
2	3	105·40	1·4680	—
3	4	97·75	1·4670	—
4	5½	83·33	1·4654	—
5	7½	71·60	1·4640	35·0
6	8½	69·39	1·4638	36·0
7	9½	63·28	1·4638	39·0
8	10½	57·68	1·4625	42·0
9	11½	55·18	1·4620	45·5

Table 4.

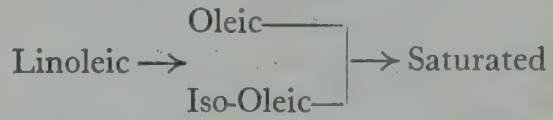
Sample No.	% Linolenic.	% Linolenic	% Oleic.	% Iso-Oleic.	% Saturated (By difference)
0	1·6	71·5	12·20	1·10	14·7
1	—	49·64	33·31	11·43	17·05
2	—	34·33	47·99	19·20	17·68
3	—	27·11	54·42	8·20	18·47
4	—	12·60	67·39	10·47	20·01
5	—	2·30	75·46	36·58	22·24
6	—	0·32	76·54	40·09	23·14
7	—	0·16	70·08	40·79	29·76
8	—	0·10	63·98	32·89	35·92
9	—	0·09	61·20	30·07	38·71

Discussion

From the result of investigation, it is seen that reaction rate is higher at high temperature as compared to reaction temperature of 150°—155°C.

It is also apparent that along with saturated fatty acid, iso-oleic acid has a definite contribution over the melting characteristics of fats.

The analytical data show that rate of conversion of linoleic acid to oleic acid is much higher as compared with oleic to saturated acid. With the gradual fall of linoleic acid concentration, concentration of oleic and iso-oleic acid increases. When linoleic acid concentration attains a very low value, hydrogenation of iso-oleic and oleic acid starts. From this, it appears that the reaction takes the following course:



The reaction conditions obtained in this experiment was repeated with a larger charge (1500 gms.) sample. It is seen from the analytical data from this experimental set, that broadly comparable figures were obtained. Selectivity performance of the second batch was better than the previous lot. This was accompanied by a little iso-acid promotion at comparable iodine value of hydrogenated oils. Keeping in view the fact that hydrogenation of vegetable oils is a complicated process, depending on various variables which control the final product, it may be said that the results obtained from two sets of experiments are in fair agreement.

The course of hydrogenation of the tobacco seed oil show that both in selectivity and iso-oleic acid formation, the trends were similar to other oleic-linoleic oils like cotton seed and pea-nut oil. It will be apparent from Table 3 that the product in the L. V. range of 69 having a slip-point 36°C has a composition similar to those found in commercial vanaspati. The following table gives a comparison between the fatty acid composition of hydrogenated tobacco seed oil and three commercial brands.

COMPARABLE FATTY ACID COMPOSITION

	Dalda vanaspati fatty acid Magar (53)	Lion vanaspati fatty acid Magar (53)	Dalda vanaspati fatty acid Mehta (54)	Hydrogenated tobacco seed oil fatty acid*	Hydrogenated tobacco seed oil fatty acid†
I. V. of oil ...	61·60	54·87	64·00	69·39	69·15
Slip-point ...	—	—	—	36°C	36·5°C
FATTY-ACID COMPOSITION					
% Saturated ...	36·25	38·14	33·10	23·14	22·45
% Total oleic ...	58·60	61·30	63·70	76·54	76·40
% Iso-oleic ...	—	—	34·10	40·19	35·40
% Linoleic (conjugatable) ...	4·83	0·062	3·20	0·32	1·15

* Hydrogenated at normal atm. press. Using 0·5% nickel catalyst.
† Hydrogenated at 5 lbs. positive press using 0·25% nickel catalyst.

It will be seen from the Table that although the iso-oleic acid percentage is more or less the same, the percentage of total oleic is about 13—18 per cent more in the tobacco seed oils and the percentage saturated acids to 10—15 per cent less than the commercial brands. It is also seen that the percentage of conjugatable linoleic acid is much less in the present samples than the commercial brands. It is clear, therefore, that while it is possible to selectively hydrogenate tobacco seed oils, it is also possible, to produce a product having more or less same proportions of iso-oleic acids, more oleic acids and less saturated acids which, from a theoretical point of view, should be more acceptable as an edible product. At the same time, the stability of the product towards oxidation is also expected to be better. It has been seen from the samples prepared that the consistency of hydrogenated tobacco seed oil is comparable to the commercial products. From the very preliminary organoleptic tests, it has been seen that these samples are acceptable as edible products. Further work regarding the nutritional aspect of these hydrogenated fats are in progress.

CONCLUSION

The use of partially hydrogenated fat requires that it should have an extended plastic range. They should be soft and plastic at room temperature and shall possess some body at temperature close to body temperature. The stability is very important since they are exposed to high temperature in baking and frying and are not usually refrigerated. Selective conditions are desirable in order to convert all linolenic and linoleic acid to stearic and oleic for maximum stability. However selectivity condition also favours the formation of iso-oleic acids. Iso-oleic acids are undesirable constituents.

They have much higher melting point than normal oleic but do not offer any improvement in the stability of the product. Further, since they are high melting, they restrict the amount of saturated acid that could otherwise be formed with greater benefit to the stability of the product. Saturated acid also serve to extend the plastic range and provide the higher temperature body required.

It will be interesting to discuss also something about the economic aspect of the problem. The following chart gives tentative comparative production cost of hydrogenated groundnut oil and hydrogenated tobacco seed oil for edible purposes.

COMPARATIVE PRODUCTION COST (TENTATIVE)

Basis : 16 tons
Product : Melting point about 36·5°C
I. V. about 69·0

	Hydrogenated Groundnut oil		Hydrogenated Tobacco seed oil	
	Actual cost	% on total cost	Actual cost	% total cost
Raw oil	Rs. 29,520	89·45	Rs. 21,632	83·20
Gas	Rs. 300	0·90	Rs. 900	3·46
Other Raw materials ...	Rs. 1,968	5·96	Rs. 1,968	7·56
Power	Rs. 320	0·97	Rs. 480	1·84
Labour	Rs. 200	0·60	Rs. 400	1·54
Other cost	Rs. 938	2·84	Rs. 938	3·60
Credit on soap stock ...	Rs. 246	0·72		1·20
Net product cost per ton	Rs. 2062.50		Rs. 1625.00	

Savings over hydrogenated groundnut oil; Rs. 437·50 per ton.

As compared to groundnut oil there is of course, a necessity of a larger amount of hydrogen gas for this highly unsaturated oil for bringing it down to the same range of iodine value and consistency. It is obvious also that for the plant of same capacity, the production rate may fall to some extent. But in as much as up to 90 per cent of the total cost is due to the raw oil, savings on this head alone will more than compensate the other factors. There is evidence that commercial hydrogenation of tobacco seed oil for industrial uses has sometimes been attempted during paucity of groundnut oil.

It may further be stated that these less known Indian Oil seeds which are obtained in plenty and are by-product of other industry, can be economically exploited to produce hydrogenated fats. In India, ground-nut oil forms the main raw material in hydrogenation industry, which is fairly costly. If the

less known oils which remained previously practically unexploited, can be used as a substitute for pea nut oil in hydrogenation industry, the more valuable and costlier ground-nut-oil, and its products can be exported to foreign countries to earn the much needed foreign exchange. On the other hand, this may further give an impetus to our indigenous tobacco industry which may find a new venue for its hitherto unexploited by-product tobacco seeds.

Acknowledgement

Sincere thanks of the authors are due to the C.S.I.R. for providing one Research assistantship (M.K.C.) and also to Prof. B. C. Guha, F.N.I. the Head of the Department of Applied Chemistry, Calcutta University for providing necessary facilities.

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PROCESSING AND UTILIZATION OF NIM AND OTHER INEDIBLE OILS

by Chitta Ranjan Mitra

*National Chemical Laboratory, Poona**

The non-fatty constituents present in the inedible oils like nim (*Melia indica*), polang (*Calophyllum inophyllum*), *Karanja* (*Pongamia glabra* vent), nageswar (*Mesua ferrae*), etc., responsible for imparting bitter taste, foul disagreeable odour and dark colour to these seed fats, render them unsuitable for any industrial use.

The non-edible oilseeds are available in plenty throughout the country, but due to lack of their proper utilization and consequent absence of organized collection and pressing of these seeds and nuts, the potential availability of these seeds and nuts cannot be properly estimated. The agricultural data published from time to time indicate these hitherto waste raw materials to be worth few million rupees.

Conventional methods of refining vegetable oils are of little value in their application to non-edible oils, and the crude soaps prepared with them in the rural areas, hardly attract the consumers.

Systematic chemical investigation in a number of non-edible oils with a view to their utilization on scientific and economic basis had been undertaken in the C.S.I.R. Laboratories and the N.C.L. as a long-range programme of research. Some of the results of these investigations having important bearing on the non-edible oil industry are briefly discussed in this paper.

The problem of utilization of non-edible oils has various facets, of which the important ones are,

(*i*) availability of the oils ;

(*ii*) suitable methods of refining and purification ; so that the pure glycerides free from foul smell, bitter disagreeable taste and dark colour, are made available for soap making, production of fatty acids and other allied industries.

Recently the Khadi and Village Industries Commission have undertaken the execution of the Planning Commission scheme for production of non-edible oils and their utilization. Different State Boards of Village Industries have already started work and an All-India Organization of Non-edible Oils Industry has been constituted ;

The problem of purification and refining of the non-edible oils has been studied in details keeping in view the following aspects :

(*i*) The complete removal of non-fatty constituents present with these oils, which are responsible for disagreeable taste, foul odour and dark colour.

* Present address : National Botanic Gardens, Lucknow.

(*ii*) Chemistry of the non-fatty constituents, their properties having direct bearing on the process of their removal from the oil and simultaneous purification of the fat.

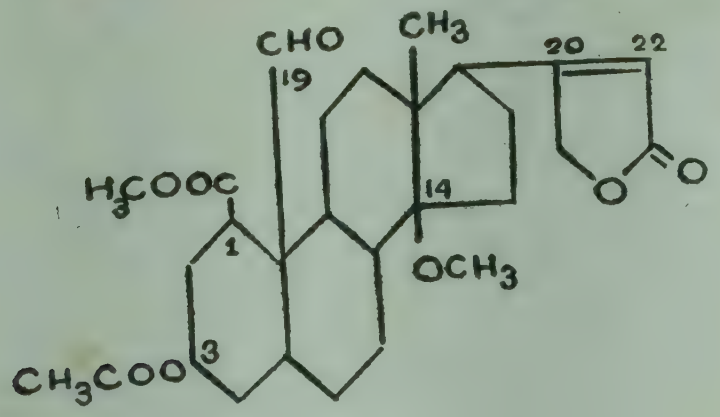
(*iii*) Fuller utilization of these resources, both of the fat as well as the non-fatty physiologically active constituents.

Taking into consideration the availability of the non-edible oil-seeds, *nim* is most extensively available and next perhaps are *karanja, undi* and *nahor* and some other minor oilseeds. *Nim, karanja, undi,* etc. are well-known as medicinal oils. But their use in medicine is of little avail due to lack of confirmation of their therapeutic values recorded in ancient literature.

Chemistry of the active principles and their medicinal properties

Active principles of nim oil

Of the three bitter constituents of nim already isolated and characterised, nimbin is a crystalline product (obtained in an yield of 0·1 per cent on the weight of the oil). From the studies in its chemistry so far carried out, it has been tentatively characterised as a cardenolide, and a provisional structure (1-carbomethoxy-3-acetoxy-14-methoxy-19-oxo-carda-20:22-enolide) has been proposed for it (I).



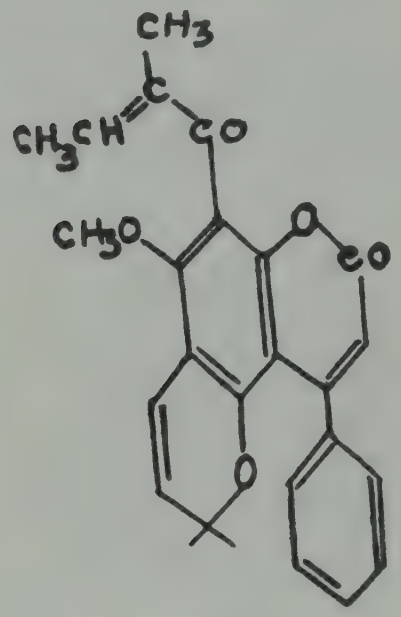
I

Nimbidin, the major bitter constituent (about 1·5 per cent yield), which is amorphous, is also closely related to nimbin in regard to the physico-chemical characteristics, oxygen functional groups and gross structural analogy. Nimbidin which is isolated in industrially workable yield from the oil, has been found to possess certain specific medicinal properties aside its efficacy in the treatment of skin affections. From the investigations so far carried out, it appears that nimbdin possesses certain specific therapeutic values. Recently, it has been reported to be active against *mycobacterium tuberculosis,* both bactericidal as well as bacteriostatic (Murthy and Sizsi, 1958). It has fungicidal properties. Its remarkable action on uterus (Siddiqui and Mitra, 1945) should be investigated to logical conclusions. Sodium nimbidinate, a derivative of nimbidin, is a promising diuretic, and clinical trials are being given with the drug in the cases of edima due to cardiac failures

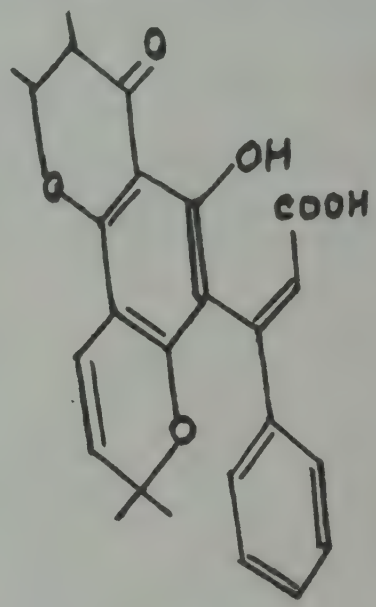
(Bhide *et al.*, 1958). The bitter constituents of nim and their derivatives are virtually non-toxic and advantage of this valuable combination of therapeutic efficacy and absence of toxicity should be fully exploited. Many of the traditional uses of nim have been substantiated by pharmacological and clinical trials so far carried out.

Active principles of undi oil

During the last few years, a number of physiologically active complex compounds have been isolated from the *Calophyllum inophyllum* nut and its oil, and their chemistry studied. A complex lactone calophylloide (II) having a 4-phenyl-substituted coumarin nucleus and a related acid, calophyllic acid (III) have been worked out in France (Polonsky, 1956). A new polyene acid,



II



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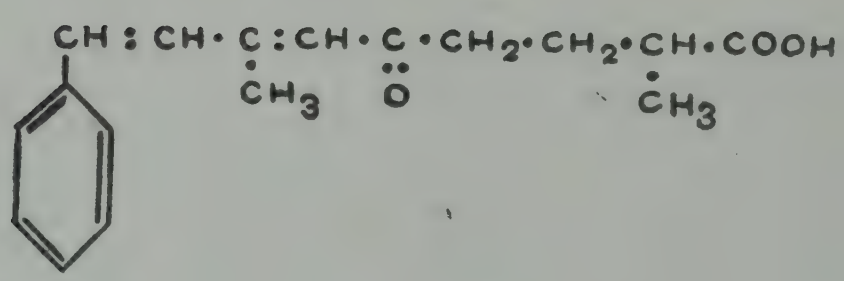
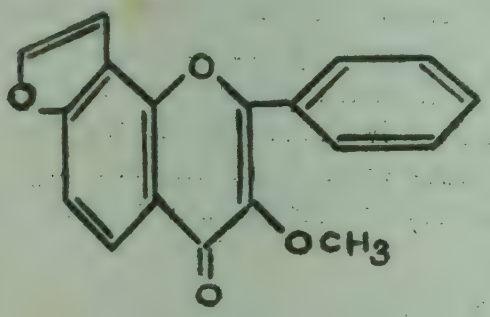


IV

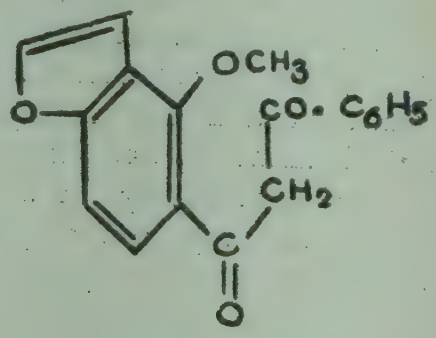
inophyllic acid (IV), has been isolated in the N.C.L. (Mitra, 1955, *b*; 1957, *b*, p. 120) and its tentative constitution worked out as ω-phenyl-2-7-dimethyl-5-oxo-nona-6:8-dienoic acid (Mitra, 1957*b*, p. 167). Calophyllolide has been found to be active against *mycobacterium tuberculosis*.

Active principles of karanja oil

Karanja oil has long been reputed to be useful in cases of leucoderma. But no systematic pharmacological and clinical work appears to have yet been carried out with the active principles of the oil, karanjin (V) and pongamol (VI) whose chemistry has been studied to a considerable extent.



V



VI

Active principle of nageswar oil

A crystalline bitter, mesuol, $C_{23}H_{22}O_5$ has been isolated from the nut (Bose *et al.*, 1940).

A review of the chemistry of the active principles present with these oils so far carried out, would show that the conventional methods of refining with alkali or mineral acids have little scope in the cases of these oils because complete removal of the non-fatty constituents cannot be ensured within the limitation of reasonable loss, and desirable quality of the resultant products. Moreover, these reagents would destroy the non-fatty constituents of therapeutic value, which could otherwise find use in pharmaceutical industry after further studies, and thus constitute substantial by-products, complementing the economics of the industrial utilization of these non-edible oils.

The process of separation of the non-fatty medicinal constituents from nim oil by extraction with dilute alcohol in cold was first adopted by Siddiqui and Mitra (1946*a, b, c,*) in the C.S.I.R. Laboratories. It had since been successfully applied in cases of other important medicinal non-edible oils (Mitra, 1953*b*) mentioned earlier. This process of purification of non-edible oils has the following outstanding advantages:

(*i*) When the glycerides are not affected (glycerides being insoluble in dilute alcohol), most of the non-fatty constituents, physiologically active bitter principles and the odorescent compounds are removed by alcohol, leaving the purer glycerides amenable to dilute alkali refining and bleaching. The refined oil thus obtained can be easily deodorized and hydrogenated (Mitra, 1957*a*).

(*ii*) The alcoholic extract of the oil is further processed and individual active principles isolated from it. This mild process ensures isolation of the

active bitter principles, nimbin, nimbidin and nimbinin, from the nim oil (Siddique and Mitra, 1945). These bitter constituents have been obtained in the native state in which they are present in the plant, which had been confirmed by their isolation from the root and trunk bark of the tree (Mitra *et al*, 1953*a*, *b*).

(*iii*) The process is simple and economic, in consideration of the fact, that (i) the equipment required is not complicated and can be fabricated locally; (ii) the solvent, rectified spirit, which is by far the cheapest of all industrial solvents in our country, employed in the process, is recovered and reused; (iii) dilute alcohol extracts considerable proportion of the free fatty acids of the oil rendering the alkali refining easier, and the refining loss is compensated to a large extent by the recovery of comparatively better quality fatty acids from the refining foot.

Extensive work has already been carried out in the National Chemical Laboratory and the results show that each of the fractions obtained as by-products in this purification and refining process can be utilized. This process has been worked out on pilot plant scale in the laboratory, and on a comparatively larger scale in collaboration with industry. The possibility of adopting this process on the village industry scale is also being explored in active collaboration with the Bombay Village Industries Board.

Refining loss. It is well-known that refining loss in case of an oil is directly proportional to the acid value of the oil. The hypothetical relation is generally shown by the equation particularly evolved in case of cottonseed oil, % refining loss $= 4{\cdot}0 + 2{\cdot}1 \times (\%\text{ffa})$ (Eckey, 1954).

The conventional acid value indicates the amount of free fatty acids present in an oil. We can put it in a modified way, i.e. the acid value indicates the amount of alkali labile products present in the oil. These alkali labile products in cases of the so-called non-edible oils are not only free fatty acids, but certain other constituents which are non-fatty. As for example, the bitter constituents as well as sulphur containing odorescent principle of nim oil are all alkali labile. More or less, similar is the case with other non-edible oils. This leads to the question of non-sap. values of these oils. Conventional non-sap. value means the amount of non-fatty products which are not saponified by or reacted upon by alkali. They are, generally, the sitosterols, a little of hydrocarbons and higher alcohols. This conventional conception of non-sap. value of an oil cannot be rigorously applicable in the cases of non-edible oils, because there are products in these oils which are non-fatty but alkali labile. What is more important, is the fact that the quantities of such non-glyceridic components present with these oils are not negligible. As for example, nim oil contains about 2 per cent of the steroidal bitter constituents and about 4 per cent of the odorescent principles. About 2 per cent of the well-defined non-fatty chemical constituents comprising of a complex lactone and a peculiar non-glyceride polyene acid have already been isolated from *undi* oil. Similar also is the case with *karanja* oil. These facts will have to be borne in mind not only to account for the refining loss but also because in-

complete separation of these components from the oils would lead to the presence of the degradation products of these constituents in the resulting soaps, rendering the finished products poorer in quality in regard to the colour, odour, taste and their 'keeping' properties.

Apart from these non-fatty constituents, comparatively larger quantities of free fatty acids are present with the non-edible oils, which would apparently add to the refining loss. An example is *undi* oil from which as much as 25-30 per cent. of the fat can be extracted with dilute alcohol, alcoholic extract consisting mostly of the free fatty acids. Nim oil would yield 8-10 per cent. or even more depending upon the age of the oil, of dilute alcohol extractable material, more than 50 per cent of which are free fatty acids.

Evidently refining losses in the cases of non-edible oils cannot be low enough to compare them with those of purer oils like the groundnut oil.

An analogy in this respect might be possible to some extent with cotton-seed oil. It thus follows, that to ensure utilization of non-edible oils on industrial scale and on economic basis, every attempt should be made to make use of the non-fatty constituents and also to recover the fatty acids from the foots in comparatively better quality so that they may find use in soap, stearin, and allied industries.

As has already been indicated, the processing of the non-edible oil-seeds and fats has certain problems inherently peculiar to them. While there is very little scope in this paper to discuss the problems of collection and processing of the non-edible seeds and nuts and production of the oils, mention may be made of a very significant property of some of these oils, having direct bearing on the storage and transport. Both *karanja* and *undi* oils have in them the non-fatty components which form dark coloured complexes with ferric ions. Evidently storage of these oils in rusted mild steel barrels causes darkening of the colour of the oils. It can be often noticed that old *karanja* oil is dirty brown in colour while fresh *karanja* oil is bright yellow. In case of *undi* oil, one can even get a sample which is dark blue in colour while fresh *undi* oil is light olive green in colour. When bleaching of purified and refined *undi* oil is not much of a problem decolourisation of *karanja* oil poses a difficult problem. Although purified *karanja* oil offers little difficulty to hydrogenation but the hydrogenated fat may retain a light brown colour. Thus due attention may be paid to the problem of storage and transport of these two oils.

Fixed glycerides of non-edible oils are composed of common fatty acids.

Systematic investigations on these oils carried out in the N.C.L. have *inter alia* clarified certain conflicting observations made by earlier workers. Some peculiar acids were reported to be component acids of the glycerides of these medicinal oils, e.g. 'margosic acid' and a C_{15}-acid in nim oil, dihydroxystearic acid in *karanja* oil, abeitic acid erucic acid in *undi* oil. These observations were mainly due to isolation of impure constituents and their incomplete characterisation. The physico-chemical characteristics of some

important non-edible oils, crude, as well as purified and refined by the processes just described are given in Table I. The fatty acids of some of these oils purified and refined, have been examined by modern methods of low temperature crystallisation and U.V. Spectrophotometry, and they have been confirmed to be common fatty acids (Table II) (Gupta and Mitra, 1953). Fatty acid composition of the pure glycerides of these non-edible oils confirm their properties to yield soaps of good quality. Amongst these oils, nim is the best in respect of its saturated acids content (figures in parentheses in Table II), and *undi, karanja* and *nageswar* compares well with the groundnut oil. Thus it is evident that the glycerides of these non-edible oil-bearing seeds are not responsible for the medicinal values attributed to these non-edible oils. Physiologically active constituents are the non-fatty components present with these seed fats.

Uses of the various products from these oils

Apart from high grade soaps, stearin and olein, high melting stearin can be produced from the purified, refined and hydrogenated nim and other oils.

The by-products obtained during the processing of non-edible oils by the methods developed under the C.S.I.R. will also find use in one way or the other as discussed in the foregoing pages, apart from in the industries employing fats as raw materials. As for instance, the fraction containing the odorescent sulphur compounds of nim oil may be of specific values for certain uses as an insect repellant.

Pyrolytic degradation product of nim oil or the fatty ballast has recently been found to be a suitable general denaturant for alcohol.

The analyses of processed seed meals of nim and nageswar show that they will be quite useful atleast as cattle feed (Mitra 1957*a* : 1957*b*, p. 120).

TABLE I

Physico-chemical characteristics of some non-edible oils.

	Karanja oil		Nim oil		Calophyllum inophyllum oil		Nageswar oil	
	Crude	Purified & refined	Crude	Purified & refined	Crude	Purified & refined	Crude	Purified & refined
Colour Lovibonds 1 cm.	42Y 22·7R	3·1Y	52Y 3·5R 0·2B	3·6Y 0·5R	40B 24·5Y 7·0R	0·9Y	28Y 5·6R	0·8Y 0·2R
Odour (characteristic)	strong	faint & non-bitter	strong disagreeable	faint & non-bitter	strong disagreeable	faint & non-bitter	strong disagreeable bitter	faint non-bitter
Sp. gr.	0·9273 (32°)	0·9033 (32°)	0·9290 (30°)	0·9087 (30°)	0·9306 (25°)	0·9081 (25°)	0·9202 (34°)	0·9064 (31°)
Refractive index	1·4774 (33°)	1·4650 (33°)	1·4785 (30°)	1·4612 (30°)	1·4760 (25°)	1·4686 (25°)	1·4721 (32·5°)	1·4651 (31°)
Iodine value	82·9 (Wij's)	87·4 (Wij's)	74 (Wij's)	66·4 (Wij's)	84·6 (Wij's)	81·8 (Wij's)	81·1 (Wij's)	76·6 (Wij's)
Saponification value	187·5	190	198	193	198·2	196·8	203·2	197·7
Acid value	7·5	0·4	8·5	0·3	13·1	0·4	8·8	0·5

TABLE II.

Component fatty acids.

Fat	Myristic	Palmitic		Stearic	Arachidic	Oleic	Linoleic	Linolenic
Melia indica (Nim) Purified and refined	0·2	16·2	(34·4)	14·6	3·4	56·6	9·0	—
Calophyllum inophyllum (Undi) or (Polang)	—	16·8	(26·5)	9·7	1·0	49·7	23·8	—
Mesua ferraea (Nageswar)	—	6·4	(22·6)	14·2	—	65·4	9·7	—
Pongamia glabra vent (Karanja)	—	7·9	(21·0)	3·7	2·5 C_{20} 4·2 C_{22} 1·1 C_{24}	62·1	11·9	5·0
Arachis hypogaea (Groundnut)	—	8·5	(19·5)	4·4	6·6	54·0	26·0	—

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SECTION D

IMPROVEMENT IN PRODUCTION METHODS

ADDUCT-FORMING PROPERTIES OF ACTIVATED UREA

by T. N. Mehta and M. S. Murty

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Abstract

Urea adduct of lauric acid was extracted with benzene in a Butt extractor for about 8 hours. The solid urea thus obtained was found to be more reactive than ordinary urea in its adduct forming tendencies. Hence it was given the name activated urea. Activated urea formed adducts with the fatty acids without the aid of any catalyst such as water or methanol.

Urea is one of the few simple organic compounds having high crystallographic symmetry. Hendricks (1928) and Mark and Weissenberg (1923) have studied the crystal structure of urea. Since hydrogen bonds provide relatively strong intermolecular forces urea forms crystalline complexes with numerous substances. The urea molecules form interpenetrating spirals round the long chain molecules. Hydrogen bonding between the adjacent urea molecules and the van der Waal's forces between the long chain and urea molecules account for the stability of the structure (Redlich *et al.*, 1950 : Smith, 1950).

All urea inclusion compounds crystallize in hexagonal prisms and generally appear in the form of thin or coarse needles. Analysis of the crystal structure revealed that the regular hexagonal prisms are built up exclusively of urea ; the six molecules forming the unit cell occupy the edges of the prism spiralling over a length of 11·1°A (Schlenk, 1954).

The honeycomb-like structure suggests the assumption that the aliphatic molecules occupy the free space inside the hexagonal channels. The cross-sectional diameters of molecules bound by urea fit well into the lumen of the prism. The maximum diameter of an extended linear hydrocarbon is close to 4·5°A, whereas the inside diameter of the channel is approximately 5·5°A. The experimental fact that molecules undoubtedly thicker than this available diameter do not form urea inclusion compounds accords with this assumption (Schlenk, 1954).

It has usually been assumed that urea will not crystallize in the pericytic (peri = around ; cytos = cell) form in the absence of a structure builder and that removal of the endocyte (endon = within ; cytos = cell) from a complex causes the urea to revert to its tetragonal structure (Truter, 1954). Preliminary experiments by McAdie and Frost (1955) indicate that the pericytic structure might exist by itself. By means of a quartz spiral balance they measured the up-take of octane vapour by solid urea. Initially no reaction took place unless the water vapor pressure exceeded 8 mm. After the complex had formed it was decomposed by pumping off the octane and then regenerated by admitting more octane, but without water vapour. On this occassion the complex was formed, but in lower yields than before. Repetition of the cycle gave the same yield as on the second occasion. These observations can be explained in two ways: either the pericytic urea struc-

ture is stable in the absence of endocyte or the microcrystalline urea residue does not require a catalyst for its reconversion. The second explanation is more likely to be correct.

The possible solvents which could be employed to dissociate adducts are (1) those which dissolve only urea (2) those which dissolve only the organic component and (3) those which are solvents for both.

An example of the action of a solvent of type (1) is given by water. As water has a very high solvent ability for urea, complete dissociation takes place with a moderate amount of water. An alternative for the recovery is the extraction of organic component using solvents of the type (2). Meade (1951) extracted wax esters bound in urea by boiling twice with benzene but Schlenk (1954) found that the extraction of palmitic acid was not complete after several hours treatment with ether in a Soxhlet apparatus. As might be expected the solvents of type (3) bring about the strongest dissociation. Nevertheless, dissociation by such solvents, even with dilution, is not always complete.

To a large degree the dissociation constant is dependent upon the molecular size of the bound organic compound. The tendency to dissociate decreases as the molecular size increases. For example, lauric acid adduct dissociates to a great extent than stearic acid adduct. As the temperature is raised, the tendency for dissociation of the adduct increases, because the lattice energy of the urea complex steadily decreases until the melting point of urea is reached at 132·7°C (Kobe and Domask, 1952).

In the present work urea adduct of lauric acid was extracted with benzene in a Butt extractor and the solid urea thus obtained was used to investigate its adduct forming tendencies with fatty acids.

Experimental

Urea adduct of lauric acid was prepared by treating it with saturated solution of urea in methanol and separated by filtering over a sintered glass funnel. The adduct was extracted with benzene in a Butt extractor for 8 hours.

Lauric acid was taken in two flasks (about 1 gm. in each) and dissolved in petroleum ether (25 ml.: B.P. 40°-60°C.). The above extracted urea was added to one of the flasks and ordinary solid urea to the other. The contents of the flasks were thoroughly agitated and kept in water at room temperature. The adducts were separated after two hours by filtering over sintered glass funnel and washed with petroleum ether. The raffinates were titrated against standard alcoholic KOH and the amount of fatty acids calculated. The experiments were repeated with myristic, palmitic and stearic acids. Results are included in Table I.

Discussion

It is evident from Table I that urea obtained after extracting the adduct with a solvent which dissolves fatty material was more reactive than ordinary urea, with respect to its adduct forming tendencies. Hence it was given the

TABLE 1.

	Lauric acid (m.wt. 201·0) a	b	Myristic acid (m. wt. 228) a	b	Palmitic acid (m. wt. 254) a	b	Stearic acid (m. wt. 272) a	b
Amount taken (g)	1·09	1·10	1·05	0·85	1·11	0·44	1·16	1·01
Urea added (g)	3·10	3·00	1·92	3·00	0·62	3·00	3·16	3·0
Time (hours)	2	2	2	2	2	2	2	2
Fatty acid in raffinate (g) calculated.	0·21	1·10	0·51	0·85	0·93	0·44	0·20	1·00
Fatty acid adducted (g).	0·88	0·00	0·54	0·00	0·18	0·00	0·96	0·01
Moles urea per mole fatty acid.	11·8	—	13·8	—	14·5	—	14·9	—
Theoritical moles urea per mole fatty acid.	10·4	10·4	11·8	11·8	13·2	13·2	14·6	14·6
Activation (c)	0·88	—	0·86	—	0·91	—	0·98	—

(a) Activated urea was used.
(b) Ordinary solid urea was used.
(c) Activation=Theoritical number of moles of urea per mole fatty acid/moles of urea required per mole fatty acid.

name "activated urea". The activated urea formed adducts, without the aid of any catalyst such as methanol or water, unlike ordinary urea.. Heating was entirely eliminated for adduct formation. Under similar conditions adduct formation with ordinary solid urea was negligible (Table I). The number of moles of activated urea required per mole of fatty acid is slightly more than the theoretical number as given by Marschner (1955) (0·× number of C atoms + 2).

The adduct forming properties of the activated urea depend upon its particle size and crystalline structure. Calderbank and Nikolov (1956) also showed that adduct formation was observable with solid urea, only when the particle size was less than a certain critical value.

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THE SEPARATION OF FATTY ACIDS USING UREA

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Abstract

The increasing use of specific individual fatty acids for definite purposes, e.g., of linoleic acid by mouth for the prevention of atherosclerosis, has led to an interest in commercially-feasible methods of separation. These methods now comprise solvent crystallisation and fractional vacuum distillation, neither of which, as commercially applied, separates unsaturated acids among themselves. The utility of the technique of urea adduction for this purpose is illustrated by data on the complete resolutions of natural fatty acid mixtures, and the variations of procedure possible. In all cases the mixtures can be separated into simpler fractions each containing predominantly one fatty acid. An interesting application of the method is the almost quantitative recovery from dark cottonseed foots of light-coloured fatty acids in two crops of low and high unsaturation. Considerations bearing on large-scale application are discussed.

Use of Specific Fatty Acids

The use of specific fatty acids in place of natural fats is yet another example of man improving on nature. Besides the obvious fact that one may use what is exactly suitable for any particular purpose, thus avoiding wastage, fatty acids can be obtained from any fatty material, edible or inedible, high-grade or low-grade. Use of only the poorer fats as sources of fatty acids, apart from economic advantages, spares the better materials for more worthy purposes. Specific fatty acids are in increasing use. The saturated acids, especially stearic, find employment in the fields of soaps, cosmetics, rubber, greases (as metal salts) and textiles, where they supply emollient, hardening or water-repellant characteristics. Oleic acid is a useful detergent base, and is used also in lubricants and carbon paper manufacture. Linoleic acid concentrates are of great potential value. With advances in the understanding of surface coatings, e.g. the alkyd resins, less reliance need now be placed on the use of drying fatty oils or acids, linolenic and elaeostearic, since functionality and cross-linking can be provided by altering the alcohol part of the molecule; for the acid part, linoleic acid provides an excellent non-yellowing product of adequate functionality. In another field, it is being widely used as such for the alleviation of atherosclerosis (deposits of cholesterol or cholesterol esters in the arteries) and eventual heart disease, incidentally leading also to a trend away from the indiscriminate hydrogenation of linoleic-rich oils intended for edible use.

Some advantages of the use of fatty acids may be illustrated by reference to soaps. A soap manufacturer using a certain proportion of stearic acid can afford to throw in a correspondingly greater range of unsaturated oils instead of being confined to just a few as at present. From the economic point of view, the glycerol that is obtained by splitting fats is a by-product so expensive that fatty acids may actually be sold at less than the price of

the parent fats. The presence of glycerol is known to result in certain defects in the soap, such as hygroscopicity and quick wasting, when prepared by the cold or semi-boiled process. This is avoided using fatty acids, while the actual neutralisation process is quicker, the bulks smaller, and salting-out, with its attendant wastage, eliminated.

Separation of Fatty Acids Mixtures

Fatty acids may be separated in several ways. One of the oldest methods employs the differential crystallisation of their metal soaps, especially lead, from alcohol or ether, but this has remained mainly a valuable laboratory tool. While the fractional distillation of fatty acid esters under vacuum has again been an important laboratory technique, the vacuum distillation of fatty acids themselves, with or without steam, has been used for commercial separation over the last twenty years. This has generally been applied in conjunction with two other techniques: hydrogenation, whereby stearic acid can be obtained from oils of any degree of unsaturation: and crystallisation from solvents at below-ambient temperatures. In the latter, while laboratory procedures have employed a variety of solvents, and temperatures down to −70°C, commercial crystallisations have generally been confined to the well-known Emersol process of crystallising the mixed fatty acids (particularly of tallow) from 90 per cent methanol at −12°C to give saturated and unsaturated acids in two groups (Demmerle, 1947).

There are limitations to each of these industrial processes. In commercial crystallisations, saturated acids as a whole crystallise out fairly completely, but individual acids are not easily separable. The unsaturated acids are obtained as a group fairly free of saturated acids, but for crystallisation of individual unsaturated acids, it is necessary to go down to very low temperatures, which has so far been confined to the laboratory, perhaps because it is uneconomic and difficult to handle large bulks of solutions at very low temperatures on a large scale. The distillation method separates acids according to chain length: thus palmitic and stearic acids are well resolved, but stearic, oleic, linoleic and linolenic acids, all with an eighteen-carbon chain, are normally inseparable by distillation.

Recently another method has become available for fatty acid separation, which, unlike certain other laboratory resolving techniques like chromatography or multiple counter-current distribution, is potentially capable of application on a large scale. The urea-adduct technique is based on the phenomenon that when urea encounters a long, straight-chain molecule, it wraps itself around the latter using residual Van der Waal forces to form crystalline products called adducts or clathrates or occlusion compounds which can be filtered off (Bengen, 1940). Urea may be present in solid form, and the reaction is very rapid and commences instantly: the presence of a mutual solvent helps adduct formation and, of course, subsequent filtration. Fatty acids are regenerated from the adducts by throwing the latter into water, preferably slightly acidulated.

Use of Urea for Separation

Since about 1951, we have been interested in the technique by reason of its ease and simplicity. Rather than studying the application of the method for specific purposes, as has been done by most other workers in the field, we worked out the complete resolutions of typical fatty acid mixtures, with the intention of ultimately applying the process on a large scale. Certain generalisations are possible from our work. The precipitation of any particular fatty acid as an adduct is not absolute, but dependent rather markedly upon the presence or otherwise of other acids. Thus linoleic acid may be precipitated if saturated and oleic acids are present, but not if fairly pure. Saturated acids are generally easily adducted, and carry down also adducted oleic acid ; a second adduction of such material leaves the oleic acid in the filtrate unadducted, reprecipitating saturated acids. Yet after repeated adductions of unsaturated mixtures, saturated acids will still remain to the extent of 2-3 per cent in the solubles. It is possible, by readducting each of the two fractions obtained by a primary adduction, to separate fatty acid mixtures into four groups with a wide range of iodine value, i.e. containing a smaller number of fatty acids, or often predominantly a single fatty acid. From almost any mixture containing saturated acids, these can be recovered admixed with about 30 per cent of oleic acid. From any mixture containing linoleic acid, all the acid can be obtained in an 85 per cent concentration as one fraction. If the original mixture contains 70 per cent linoleic acid, as does that from safflower oil, a fraction comprising half the total can be had in which the acid forms 90 per cent. Resolutions of a few typical mixtures are shown in Table 1 (Achaya *et al.*, 1955*a*).

Table 1.

Separation of fatty acids from various oils using urea.

Fraction	Groundnut Oil		Cottonseed Oil		Safflower Oil		Linseed Oil	
	%	I.V.	%	I.V.	%	I.V.	%	I.V.
A	17	27	25	31	10	30	15	55
B	21	68	20	101	11	90	21	152
C	28	92	18	126	35	140	12	175
D	34	143	37	166	44	176	52	237

Table 2.

Urea resolutions of fatty acids in various media

(a) *Cottonseed oil mixed fatty acids*

Fraction	Urea in satd. Methanol		Urea in satd. 80% Ethanol		Solid Urea Method I		Solid Urea Method II	
	%	I.V.	%	I.V.	%	I.V.	%	I.V.
A	25	31	17	17	25	40	14	24
B	20	101	21	75	24	96	18	78
C	18	126	18	100	24	107	19	93
D	37	166	44	152	27	166	49	144

(b) *Safflower oil mixed fatty acids*

Soluble fraction from a single urea adduction	44	176	73	165	40	172	—	—

As mentioned earlier, urea can be used even as a solid ; in laboratory studies a modicum of ethanol is used for fluidity and convenience in filtration. It can also be used in saturated solution in methanol, or in 80 per cent ethanol (in which the solubility of urea is the same as that in methanol). The resolutions by these three media have been thoroughly studied with various mixtures (Achaya *et al.*, 1955*a*), but only the results for cottonseed oil fatty acids are presented in illustration (Table 2). It can be seen that urea in methanol is the most selective in resolving both saturated and unsaturated ends, the most saturated acid fraction having the lowest I. V. and the most unsaturated the highest I. V. compared to the other media tried ; it is excellent for laboratory work. Urea in 80 per cent ethanol is less selective. Urea as solid is a flexible medium, and the degree and nature of the separations can be regulated simply by adjusting the quantity of urea used ; the bulk to be handled is less than when urea is employed in saturated solution.

Very recently a further step forward has been made (Subrahmanyam and Achaya, 1957). While urea adduction with saturated acids is almost instantaneous, a lag period exists with unsaturated acids, particularly linoleic. By adducting rapidly the fatty acids from safflower oil, it is possible to leave in solution 98 per cent linoleic acid in a yield of 64 per cent. Extending this principle further, a two-way flexibility has been obtained by adjusting both the amount of urea used and the time of adduction. It may ultimately be possible to resolve most fatty acid mixtures into their individual component fatty acids, and work is in progress in this regard. It is at least certain that urea adduct separations can resolve to a considerable degree unsaturated acids among themselves, which by existing commercial methods is not possible.

Cottonseed Foots

Another application of the urea adduct technique may be mentioned. The material obtained by acidifying the dark foots produced in refining cottonseed oil contains fatty acids, colouring matters, etc. Since urea rejects polymers, the fatty acids may be obtained in 85 per cent yield by creating adducts with the material, filtering, washing, and regenerating fatty acids, which are pale in colour and obtained moreover in two groups of I. V. 60 and 130 respectively, each specifically useful (Achaya *et al.*, 1955*b*).

Large-scale Working

Some considerations bearing on large-scale working may be discussed. Laboratory work has shown that the alcohol employed for imparting fluidity is recovered to the extent of 85 per cent ; in large-scale work, this would be higher. To obtain complete release of fatty acid from the adduct, it is necessary to decompose it not with water but with 1 per cent hydrochloric acid ; the urea obtained by evaporating this slightly acid solution is re-usable, and of course fully recovered. Pilot-plant working data for urea

separation of petroleum has been reported in one communication in the U.S.A., and it is also believed to be used commercially. None is available for fatty acids. The economics of the process can only be obtained by pilot-plant working, and a scheme for the purpose is being implemented. The process to be employed is not the same as the extractive crystallisation process of the petroleum pilot plant mentioned earlier, but is based on a simpler technique worked out at the Laboratory. The fatty acids needed in large quantities for the work will come from the fat-splitting unit which been installed as part of the 100 kg. batch fatty acid distillation plant. By coupling the urea technique with standard processes of solvent crystallisation, hydrogenation and fatty acid distillation, individual fatty acids, both saturated and unsaturated, can be produced in India.

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UTILIZATION OF SPENT NICKEL CATALYST FROM VANASPATI INDUSTRY

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Abstract

Several hundred tons of spent nickel catalyst (nickel mud) is allowed to go to waste by the Vanaspati industry every year. As nickel is a costly metal and has to be imported, the recovery of the spent nickel catalyst is of great importance. The paper deals with a practical method for recovery of the spent catalyst.

Samples of spent catalyst from several hydrogenation factories have been analysed and found to contain 42·2% to 84·2% of fat, 7·0% to 11·3% of nickel and 7·0 to 47·4% of insoluble matter.

Following 3-methods have been tried for recovering adhering fat from spent nickel catalyst.

(1) Extraction with solvent and centrifuging.
(2) Extraction with solvent, settling and filtration.
(3) Digestion by an acid.

Fat recovered by the first two methods is of better quality than the fat recovered by the last method. But the method of digestion with formic acid is most suitable from the point of view of recovery of the spent catalyst.

The method of acid digestion consists in heating the spent catalyst at 105°C with dilute mineral acid or formic acid for a few hours while keeping it stirred. The fat which separates and floats on the surface is extraced with a solvent. The solution is then filtred, the filtrate containing the nickel in solution.

In case of digestion with formic acid the impurities of iron and aluminium are removed by precipitating them as their hydroxides.

The nickel formate obtained above compares favourably with the imported one as regards its catalytic activity in the process of hydrogenation.

The present installed capacity of the Vanaspati industry in India is about 4·5 lac tons per annum. At present the industry produces about 270,000 tons of Vanaspati annually consuming about 275 tons of nickel formate as catalyst. With the development of the industry in the near future, the demand for nickel formate may go up to 400 tons valued at about 25 lacs of rupees. About 200 tons of spent nickel catalyst (nickel mud) forms an industrial waste of Vanaspati industry annually. Work on recovery of nickel from the spent catalyst has been done in foreign countries as well as in India and it has been found that it contains a good amount of adhering fat, siliceous matter and nickel. As there are no nickel ore deposit in India and as the demand of nickel formate is likely to increase with the increasing industrialisation of the country, the recovery of nickel from spent nickel catalyst for its reuse in the industry appears to be important.

Several methods have been studied so far for the recovery of nickel from spent nickel catalyst, viz. (a) Incineration (Morrison) (b) Saponification (Kaminskii and Ellis 1930) (c) Solvent extraction (Vis, 1919; Omiya and Suzuki, 1920) of the fat followed by treatment of the residue with mineral acids., (d) digestion with mineral acid (Kinnura, 1936 and I. C. I., 1940, 1942) (e) digestion with formic and acetic acid (Bharucha, Kane and Rebello, 1957). Belekar, Kane, & Shahani (1952), worked on the spent nickel catalyst and recovered 93-98 per cent nickel by digesting the spent catalyst with sulphuric and nitric acid mixtures. Bhasin, Gupta, and Aggarwal, (1952) developed

a method for the recovery of both nickel and fat from the spent catalyst by digesting it with dilute hydrochloric acid and removing the impurity of iron by precipitating it as hydroxide. Bijawat, and Bedekar (1954) worked out a method for large scale recovery of nickel and fat from spent catalyst. The nickel was recovered as nickel sulphate by digesting the spent catalyst with dilute sulphuric acid and the acid digest was neutralised with sodium carbonate. Hydrogen peroxide solution (3 per cent was used for oxidising iron to ferric state. Bharucha, Kane, & Rebello, (1957) recovered nickel upto 90 per cent from the spent catalyst by digesting it with mineral acids and upto 92·6 per cent by digesting it with formic acid and reactivated the recovered nickel and studied its catalytic activity by performing hydrogenation trials on pilot plant scale. Sharma, Bhatnagar, & Kuloor, (1958) found out a method for recovering fat, by using solvent (mixture of benzene and ethanol) and nickel by treating the oil free residue with dilute sulphuric acid (9 per cent).

The present work was undertaken for further study of the problem.

Experimental

Analysis :

Four samples of spent nickel catalyst were obtained by the courtesy of the hydrogenation factories in U. P. They were first analysed as under:—

About 10 gms. of each sample of spent nickel catalyst were digested with dilute sulphuric acid (16 per cent keeping the contents heated (105°C) and stirred. After thorough digestion the contents were cooled and extracted with petroleum ether several times to recover the fat. The ether is distilled off and the residual fat is weighed. The contents left after extraction with petroleum ether were filtered and washed with hot distilled water to recover the last traces of nickel sulphate from it as tested by dimethylglyoxime method. The filtrate and washings containing nickel sulphate along with impurities is made to known volume. An aliquot part of the solution was then analysed for nickel content by dimethylglyoxime method and aluminium and iron were determined by precipitation and colorimetric method. The results are given in the following table:—

Table I

	Sample 1	Sample 2	Sample 3	Sample 4
Moisture	0·7	0·8	0·7	0·65
Fat %	52·5	42·2	44·4	84·25
Insoluble matter % ...	37·6	47·4	42·5	7·05
Nickel (Ni %) ...	8·7	8·5	11·3	7·0
Aluminium (Al %) ...	0·06	0·05	0·03	0·04
Iron (Fe %)	0·40	1·00	0·35	0·50

Recovery of Fat from the Spent Nickel Catalyst

The following three methods were used for recovering adhering fat from each of the samples:—

(*i*) Extraction with solvent and centrifuging and filtration.

(*ii*) Extraction with solvent, settling and filtration.

(*iii*) Digestion by an acid.

Spent nickel catalyst was shaken in different solvents and subjected to to first two processes. The results of the methods are given in the following tables:—

TABLE II

Extraction of fat by centrifuging. Speed of Centrifuge—4000 r.p.m. Ratio of the mass of the solvent to the mass of spent catalyst (2 :1).

Serial No.	Solvent	Spent Catalyst	Time. Centri-fuging. Mts.	No. of Extrac-tions	Fat %	Remarks.
1.	Pet. ether B.P. 60-80	S. 1	5	4	51·0	Miscella & Residue separated clearly.
2.	,, ,,	S. 2	5	4	41·3	,,
3.	,, ,,	S. 3	3	—	—	Clear separation did not occur.
4.	,, ,,	S. 4	5 & 10 & 20	—	—	,,
5.	,, ,,	S. 3	10	4	42·9	Clear separation took place.
6.	Mixture of Benzene 67%, ethanol 33% by vol.	S. 1, S. 2, S. 3 & S. 4	15	—	—	Clear separation did not occur.
7.	Commercial benzene	S. 1	10	4	50·8	
8.	,,	S. 2	10	4	41.0	
9.	,,	S. 3	10	4	43·0	
10.	,,	S. 4	20	—	—	Fine black colloidal particles remained in suspension.

TABLE III

Extraction of fat by settling & filtration
Ratio of the mass of the solvent to the mass of spent catalyst (3 :1)
No. of extractions 4

Serial No.	Solvent	Spent catalyst	Settling time. Hrs.	Fat %	Remarks.
1.	Pet. ether, B.P. 60-80°C.	S. 1	8	50·9	
2.	,,	S. 2	8	40·2	
3.	,,	S. 3	4	41·0	
4.	,,	S. 4	20	—	Clear separation of miscella and the residue could not occur.
5.	Mixture of benzene 67% & ethanol 33% by vol.	S. 1	18	49·5	
6.	,,	S. 2	18	40·1	
7.	,,	S. 3	10	39·8	
8.	,,	S. 4	20	—	Clear separation of miscella and the residue could not occur.
9.	Commercial benzene	S. 1	12,	50·2	
10.	,,	S. 2	12	40·8	
11.	,,	S. 3	6	42·8	
12.	,,	S. 4	20	—	Clear separation of miscella and the residue could not occur.

The recovered fat obtained by extracting with petroleum ether by centrifuging gave the following results as given in table IV.

TABLE IV

Serial No.	Spent Catalyst	Lovibond colour reading ¼″ cell y+5 R	B.R. 40°C	M.P. °C	Acid Value	Remarks.
1.	S. 1	1·2	50·5	40	0·17	—
2.	S. 2	1·3	50·5	34	0·19	—
3.	S. 3	6·65	53·0	25	1·08	—
4.	S. 4	—	—	—	—	Clear fat was not recovered.

ACID DIGESTION OF SPENT NICKEL CATALYST

Each of the four samples of spent catalyst as shown in the following table was digested with dilute sulphuric acid and formic acid separately (with required strength and excess) in a round bottomed flask fitted with a condenser and stirrer. The temperature of 105°C was maintained during digestion, and the contents of the digester were kept well stirred. Nickel and the metallic impurities of the spent catalyst reacted with the acid to form corresponding metallic salts. After the reaction was completed, the contents in the digester were diluted with water (100 gm.), stirred and decanted. Further quantity of water (100 gm.) was added to the residue left in the digester and again stirred for about 15 minutes at a temperature of 90°C. Any quantity of nickel formate or sulphate remaining in the fatty residue was dissolved in water which was again decanted off. Again further quantity of water (100 gm.) was added to the residue in the digester and stirred again as before. The contents of the flask were finally filtered and the solutions were collected together, and nickel contents in the solution determined. The results are given in table V. The fatty residue on the filter paper was extracted with petroleum ether to recover fat. Characteristics of the fat obtained have been given in table VI.

TABLE V

Wt. of spent catalyst digested—100 gms.

Spent Catalyst	Acid used	Nickel %	Excess acid %	Strength Acid %	Time Digestion hrs.	Nickel. Recovery on basis of nickel content in the filtrate.
S. 1	Sulphuric	8·7	5	15-16	3	95·2
S. 2	-do-	8·5	5	15-16	3	95·3
S. 3	-do-	11·3	5	15-16	3	98·1
S. 4	-do-	7·0	5	15-16	3	90·0
S. 1	Formic	8·7	60	20	4	95·2
S. 2	-do-	8·5	60	20	4	95·3
S. 3	-do-	11·3	60	20	4	97·7
S. 4	-do-	7·0	60	20	4	88·0
S. 1	-do-	8·7	5	20	4	95·0
S. 2	-do-	8·5	5	20	4	95·1
S. 3	-do-	11·3	5	20	4	97·4
S. 4	-do-	7·0	5	20	4	87·0

Table VI

Serial No.	Spent catalyst.	Lovibond colour reading ¼″ cell Y+5R.	B.R. at 40°C	Melting point °C	Acid Value.
1.	S. 1	1·6	50·5	40	4·4
2.	S. 2	2·4	50·4	34	5·1
3.	S. 3	10·1	52·0	25	5·9
4.	S. 4	7·5	—	50	5·5

Removal of the Impurities

As the nickel is required in the form of nickel formate in the Vanaspati industry, further work was done only for its recovery as Nickel formate. The solution of nickel formate obtained by digestion with formic acid was concentrated to 120 c.c. Impurities of iron (ferrous) were oxidised by adding hydrogen peroxide and just a small amount of basic nickel carbonate was added to the solution and then it was boiled for 10-15 minutes. The impurities of iron and aluminium were precipitated as their hydroxide and any slight acidity due to formic acid was neutralised by the basic nickel carbonate. The solution was filtered and the clear filtrate was allowed to be evaporated on a water bath for crystallization. The crystalliized mass of nickel formate was further purified by treatment with rectified spirit (95 per cent). It was observed that washing with rectified spirit definitely improved the appearance of the nickel formate. The nickel formate was finally dried and ground. The prepared nickel formate was analysed and found to be free from impurities.

Practical Trial of the Nickel Formate Recovered

Prepared nickel formate was tried side by side with imported nickel formate (technical grade). They were reduced in refined groundnut oil (iodine value 90) under similar conditions. The reduction of the formate was done at 220°C at atmospheric pressure in the presence of hydrogen. Hydrogenation trials in each case were done by taking 0·7 per cent nickel on the weight of the oil hydrogenated. Hydrogenation was carried out at 210-220°C for seven hours at ordinary atmospheric pressure. The melting point of the products in the two cases are given in Table VII, from which it will be evident that the recovered nickel catalyst compares favourably with the imported one.

Table VII

Hours	M.P. of hardened product using recovered nickel formate. °C	M.P. of hardened product using imported nickel formate. °C
1.	24	26
2.	26	27
3.	26·5	27·5
4.	27	28
5.	28·5	29·5
6.	29·2	30·5
7.	30	32

Discussion and conclusion

From the Table II and III it is clear that the petroleum ether is the best solvent for extracting the fat from the spent catalyst. The fat recovered by using petroleum ether is of better colour than that obtained by using mixture of benzene and ethanol as reported by Sharma, Bhatnagar, and Kuloor (1958). Although centrifuging is actually better, yet settling appears to be more feasible commercially. Digestion with sulphuric acid gives a slightly high recovery of nickel than digestion with formic acid. With slightly high recovery of nickel is from 87 to 97 per cent depending upon the nature of the spent catalyst.

As the nickel is required in the form of nickel formate, it appears better, to obtain the recovered nickel in this form.

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SECTION E

PHYSIOLOGY AND BIOCHEMISRTY

STUDIES ON THE PROCESSING, STORAGE AND NUTRITIVE VALUE OF COTTONSEED OIL

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Abstract

1. The proportion of linters and kernel in the nine Indian varieties are slightly lower than those reported for American varieties. The oil content of whole seeds and kernels ranged from 14 to 19·4 per cent and 29 to 35 per cent respectively which are slightly lower than those reported for American varieties.

2. Alkali refining of crude cottonseed oil yielded an oil with a light colour. Re-refining of the oil improves the colour to an appreciable extent. Bleaching of the refined oil with a mixture of Fuller's earth and vegetable carbon resulted in a very light coloured oil (0·8 Red ; 3·8 Yellow Lovibond units).

3. Crude cottonseed oil is very stable even when stored in metal vessels and this may be due to the presence of gossypol which is known to have antioxidant activity and due to the phosphatides which are found to have metal deactivation property. Refined cottonseed oil developes peroxides rapidly.

4. Winterized cottonseed oil was prepared by keeping bleached cottonseed oil at a temperature of 40-43°F for a period of 5 days and separating the solid stearine fraction. Winterized cottonseed oil was found to contain more of tocopherol than bleached cottonseed oil.

5. No significant difference between the growth promoting value of crude, refined and hydrogenated cottonseed oil, refined groundnut oil and cow's ghee was observed.

6. Crude, refined and hydrogenated cottonseed oils were found to be almost completely digestible in rat.

7. About 70-75 per cent of calcium and 65-70 per cent of phosphorus was utilized in the case of rats fed with crude, refined and hydrogenated cottonseed oils.

Considerable interest has been evinced in India during recent years in the processing and utilization of cottonseed oil for edible purposes. Crude cottonseed oil obtained from steamed cottonseed kernels has a dark brown colour and contains gossypol which is toxic (Osborne and Mendel, 1917). Consequently, unlike other oils like groundnut, coconut and gingelly oils, the cottonseed oil cannot be used for edible purposes without preliminary refining. In any programme for the utilization of cottonseed oil, data on the physical and chemical composition of cottonseeds grown in the country should be a primary requisite. Apart from the work of Desikan and Murthy (1953) no information is available regarding the composition of different varieties of cottonseeds grown in India. Though cottonseed oil is being used for edible purposes since a long time comparatively little work has been reported in the literature on the keeping quality and nutritive value of cottonseed oil. The investigations described in this paper deal with the following aspects of the problem (i) the physical and chemical composition of nine varieties of cottonseed (ii) the refining and bleaching of crude cottonseed oil (iii) the keeping quality of crude, refined and refined and bleached cottonseed oil (iv) winterization of cottonseed oil and (v) the nutritive value of crude and refined cottonseed oil.

Composition of different varieties of cottonseed

Representative samples of nine varieties of cottonseed grown in major cotton growing states in India were obtained through the agricultural depart-

ments of the respective states. The delinting was carried out by means of a rice huller which gave satisfactory results. For dehulling, the seeds were broken in a disintegrator using a 12 mesh sieve and the broken mass was sifted through a 20 mesh sieve. Whole cottonseeds were also analysed for moisture, nitrogen and fat according to the methods of the Association of Official Agricultural Chemists (1950), and gossypol according to the method of Pons and Guthrie (1949). The results are given in Table I.

Refining and bleaching of cottonseed oil :

Crude cottonseed oil obtained by expressing steamed cottonseed kernels was very dark in colour and had an acid value of 2·5. The oil was first degummed by washing with hot water to remove the impurities such as phosphatides and gummy or mucilagenous substances. This step is necessary since degumming decreases the refining loss. The degummed cottonseed oil was refined according to the official methods of A.O.C.S. (1946). For re-fining the oil 750 g. of the refined oil was treated with 6ml. of 25 per cent sodium hydroxide and was agitated at 1500 r.p.m. at 50°C for 15 minutes (Bhasin and Aggarwal, 1953). After standing overnight, the oil was decanted and was washed with hot water until free from soap. The re-refined oil was then bleached with a mixture of Fuller's earth and vegetable carbon. Vegetable carbons prepared from groundnut hull, cottonseed hull and saw dust, after activation with calcium oxide, calcium chloride and zinc chloride and some activated indigenous kaolinic clays were found to be as effective as imported earths and carbons for bleaching cottonseed oil (Krishnamurthy and Narayana Rao, 1954). The colour of the bleached cottonseed oil was found to be 0.8 Red and 3.8 Yellow Lovibond units (1 cm. cell).

Gossypol content of crude and refined cottonseed oil :

The gossypol content of crude and refined cottonseed oil was estimated by the method of Pons *et al.* (1951). In the case of crude cottonseed oil, the gossypol content varied from 0·38--0·47 per cent. Refining of cottonseed oil completely removed the gossypol.

Keeping quality of cottonseed oil :

To study the keeping quality of the oil, crude, refined and bleached samples of cottonseed oil were stored in aluminium, tinned brass and glass containers both at room temperature (25--30°C) and at 37°C. Such a procedure was adopted as edible oils are usually stored in aluminium and tinned brass containers. Groundnut oil was also included in the study for comparison. The rate of development of peroxides was followed for a period of 3 months. The results are given in Table II.

Winterization of cottonseed oil :

A sample of crude cottonseed oil was refined and given a light bleach according to the procedure described by Narayana Rao and Kuppuswamy (1953). The bleached oil was kept in a cold chamber maintained at 40--43°F for a period of 5 days during which the solid stearine fraction separated

out. The winterized oil was decanted and then filtered at the same temperature. The yield of winterized oil was 76 per cent of the refined and bleached oil. The various physical and chemical constants and the 'cold' test of the winterized oil as well as that of the original refined cottonseed oil were determined according to the standard methods of the American Oil Chemists Society (1946). Total tocopherol was estimated according to the method of Emmerie and Engel as modified by Parker and McFarlane (1940). Results of these determinations are presented in Table III.

Nutritive value of cottonseed oil :

Studies on the following aspects of the nutritive value of crude, refined and hydrogenated cottonseed oil were carried out. (i) the growth promoting value (ii) *in vivo* and *in vitro* digestibility and (iii) the effect on calcium and phosphorus metabolism.

Growth promoting value of crude, refined and hydrogenated cottonseed oil.

Five groups of six freshly weaned rats, weighing about 40 g. (distributed equally according to sex and litter mates) were fed for a period of 6 weeks on the experimental diets containing crude, refined and hydrogenated cottonseed oils, cow's ghee and groundnut oil. The composition of the diet is shown in Table IV. In addition to the diet each rat received two drops of adexoline and 2 mg. of alpha-tocopherol twice a week to meet their vitamin A, D & E requirements. The feeding was carried out for a period of six weeks. The average weekly increase in weight as well as the increase in weight per gram of fat intake is given in Table V. No significant difference was observed between the growth promoting value of cottonseed oil, groundnut oil and cow's ghee.

Digestibility of crude and refined cottonseed oil :

The *in vitro* digestibility of crude and refined cottonseed oil was studied using castor seed and pancreatic lipases according to the procedure of Ahmed and Sareen (1945-46) and Weinstein and Wynne (1935-36). The course of hydrolysis of crude and refined cottonseed oil was nearly the same as that of groundnut oil.

The digestibility coefficients of crude, refined and hydrogenated cottonseed oil were determined on adult rats by feeding diets containing the different fats at 10 per cent level. The method adopted was similar to that of Narayana Rao and De (1951). The composition of the diet is given in Table VI. Calculation for digestibility coefficients were made in the usual manner after correction for metabolic fat. The results presented in Table VII show that all the fats tested are almost completely digestible in rats.

Effect of crude, refined and hydrogenated cottonseed oil on calcium and phosphorus metabolism in young rats.

The effect of crude, refined and hydrogenated cottonseed oil on utilization of calcium and phosphorus in young rats was determined both by metabolism study (Narayana Rao and De, 1952) and by estimation of body calcium

TABLE I

Composition of Indian cottonseed

Constituent		Indian variety	American variety
Seed index	...	4·8— 8·6	10·0—11·0
Linters %	...	9·2—13·8	11·0—17·0
Hull %	...	36·0—44·0	36·0—43·0
Kernel %	...	44·0—50·8	44·0—52·0
Moisture %	...	6·7—10·7	6·7— 7·9
Protein %	...	16·8—20·9	20·0—23·0
Fat %	...	13·9—19·4	18·0—23·0
Gossypol %	...	0·8—1·6	0·9— 1·7

TABLE II

*The effect of storage in metallic containers on the development of rancidity in cottonseed oil**

(Peroxide value (millimols of thio/Kg.) after storage for 3 months)

Containers	Crude cottonseed oil		Refined cottonseed oil		Refined & Bleached cottonseed oil		Crude groundnut oil	
	Room** temp.	37°C	Room** temp.	37°C	Room** temp.	37°C	Room** temp.	37°C
Glass ...	1·5	2·8	51·0	165·0	62·0	175·0	2·9	15·0
Aluminium ...	2·2	3·6	125·0	225·0	148·0	242·0	16·0	22·0
Tinned Brass ...	2·5	3·4	126·0	230·0	139·0	245·0	14·0	25·0

* Initial peroxide value of the oil was zero; ** 25°—30°C.

TABLE III

Characteristics of refined and bleached and winterized cottonseed oils

Constituents.	Refined and bleached cottonseed oil	Winterized cottonseed oil
Colour @ ...	12·5 Y : 1·1 R	12·0 Y : 1·0 R
Iodine value ...	105·3	109.2
SCN value ...	65·8	68·1
Linolein % ...	48·8	50·8
Olein % ...	24·2	25·0
Saturated glycerides %	27·0	24·2
Total tocopherol % ...	75 mg	87 mg
Cold test	—	8 hrs.

@ Lovibond units 1 cm cell.

TABLE IV

Percentage composition of experimental diets

Extracted skimmed milk powder	20%
Extracted food yeast	16%
Chopped cane sugar	10%
Vitaminized starch	5%
Salt Mixture (Ca & P free)	4%
Agar Agar	1%
Corn Starch	35%
Fat	10%

TABLE V

Growth promoting value of crude, refined and hydrogenated cottonseed oil

(duration of experiment—6 weeks)

Fats fed	Average increase in weight per week (g)	Increase in weight per g. of fat intake
Crude cottonseed oil ...	15·35	2·31
Refined cottonseed oil	15·48	2·31
Hydrogenated cottonseed oil	14·38	2·18
Cow's ghee	15·98	2·42
Refined groundnut oil ...	14·40	2·41

TABLE VI

Percentage composition of experimental diets

Casein (extracted)	18%
Salt Mixture	4%
Vitaminised Starch	5%
Sugar	10%
Agar Agar	1%
Corn Starch	52%
Fat	10%

TABLE VII

Digestibility of crude, refined and hydrogenated cottonseed oil

Fat Fed	Coefficient of digestibility
Crude cottonseed oil	97·5
Refined cottonseed oil	97·6
Hydrogenated cottonseed oil (M.P. 37°C) ...	93·5
Cow's ghee	95·0
Refined groundnut oil	95·9

TABLE VIII

Effect of crude, refined and hydrogenated cottonseed oil on the utilization of calcium and phosphorus in young rats.

Fat fed	Metabolism study		Body calcium method	
	% Ca Utilized	% P Utilized	% Ca retained	% P retained
Crude cottonseed oil ...	74·7±3·1	66·7±2·5	67·5±2·4	62·6±2·1
Refined cottonseed oil ...	79·5±3·3	68·3±3·4	71·5±2·8	65·4±3·4
Hydrogenated cottonseed oil	71·1±2·8	61·0±3·0	72·4±2·6	53·4±2·6
Cow's ghee	83·2±2·9	65·4±2·6	76·8±2·7	58·4±2·9
Refined groundnut oil ...	76·2±2·1	59·2±3·2	66·2±2·4	54·2±2·1

and phosphorus (Sur and Subrahmanyan, 1952). The composition of the diet is the same as is given in Table IV. During the 3rd and 4th weeks of feeding during the growth study, the excreta were collected and by estimating the calcium and phosphorus excreted in both urine and faeces, the effect of different oils on the utilization of calcium and phosphorus was determined. The results are given in Table VIII. After the feeding period of 6 weeks was over the rats were sacrificed and the body calcium and phosphorus was estimated. From the amount of calcium and phosphorus retained in the body the effect of different oils on calcium and phosphorus utilization was determined. The results given in Table VIII show that there was very little difference in the retention of calcium and phosphorus in growing rats fed on diets containing the different fats.

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CHEMICAL COMPOSITION, KEEPING QUALITY AND NUTRITIVE VALUE OF SAFFLOWER AND NIGERSEED OILS

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Abstract

1. One variety each of safflower seed and niger seed were examined with respect to chemical composition of the seed, kernel and oil.
2. The stability of crude, refined and bleached safflower seed and niger seed oils was studied both by the A.O.M. test as well as by storing in aluminium and tinned brass containers for a period of three months and following the rate of development of peroxides.
3. The results indicate that safflower seed and niger seed oils are easily susceptible to oxidative rancidity and are not as stable as groundnut oil.
4. No significant difference between the growth promoting value of safflower seed oil, niger seed oil, groundnut oil and cow's ghee was observed.
5. Safflower seed and niger seed oils were found to be almost completely digestible (to the extent of 95-98 per cent) by rat.
6. In the case of young rats fed on an adequate diet containing safflower or niger seed oils at 10 per cent level the retention of nitrogen was about 51 per cent, of calcium 60-62 per cent and of phosphorus 66-67 per cent.

Safflower (*Carthamus tinctorius*) and Niger (*Guizota abyssinica*) have been known as oil seed crops of considerable importance since ancient times. They are cultivated to some extent in many states in India and have attained considerable importance as oil seed crops in Bombay and Mysore states. Both safflower seed oil and niger seed oil are classed as semi drying oils and serve as a vehicle for paints, varnishes and enamels and in the production of oil modified alkyd resins. Various investigators (Vidyarthi 1943; Bickford *et al.*, 1943, Sahasrabudhe and Kale, 1937; Hilditch and Sime, 1944) have reported data for the characteristics and fatty acid composition of safflower seed oil and niger seed oil of various origin. Although the oils have been used for edible purposes for many years, little information is available in literature about their keeping quality and nutritive value. The present paper deals with the composition, stability and nutritive value of crude and refined safflower seed oil and niger seed oil.

Experimental

Preparation and extraction of the seeds:

Healthy safflower and niger seeds obtained from Bombay and Mysore states respectively were first crushed either in a triple roller mill or a meat mincer and then steamed at atmospheric pressure for half an hour, and the oil was then expressed at a pressure of 1·25 tons per sq. in. in a hydraulic press (Laboratory model). The yield of the oil was about 20-25 per cent of the seed. However, considerable oil was lost on account of the presence of hulls along with meats.

The whole seeds and kernels were analysed for proximate principles and minerals according to the methods of A.O.A.C. (1950). The results are given in Table I.

Characteristics and composition of the oils:

The physical and chemical characteristics of the oil were determined according to the official methods of the American Oil Chemists' Society (1946). The saturated fatty acids were determined by the Bertram oxidation method. The glyceride composition of the safflower and niger seed oils was calculated from the thiocyanogen and iodine values. The results of these determinations are given in Tables II and III.

Refining and bleaching:

Crude safflower seed and niger seed oils were refined by official A.O.C.S. (1946) methods for soyabean oil. The refining was normal in all respects except that the soap stock was partly liquid even at 15°C. Losses of 3-3·5 per cent were obtained on refining with 14° Be sodium hydroxide. The colour of refined safflower seed oil was 20 yellow and 1·6 Red Lovibond units, while the colour of refined niger seed oil was 10 yellow and 1·4 Red Lovibond units. Bleaching with 2 per cent fuller's earth gave very light coloured oils.

Stability of crude, refined and bleached safflower seed and nigerseed oils:

The stability of crude, refined and bleached safflower seed and niger seed oils was studied by the active oxygen method (A.O.C.S. 1945). The results are given in Table IV.

To find out the keeping quality of the oils, crude, refined and bleached samples of safflower seed and niger seed oils were stored in aluminium and tinned brass containers both at room temp. and 37°C. Such a procedure was adopted as edible oils are usually stored in aluminium or tinned brass vessels. Groundnut oil was also included in the study for comparison. The peroxide value of the different oils was followed for a period of 3 months. The results are given in Table V.

Nutritive value of safflower seed and niger seed oils:

Studies on the following aspects of the nutritive value of safflower seed and niger seed oils were conducted (i) the growth promoting value (ii) *in vivo* and *in vitro* digestibility and (iii) the effect on nitrogen, calcium and phosphorus metabolism.

Growth promoting value of safflower seed and nigerseed oils:

Groups of freshly weaned rats, about four weeks old, weighing about 40 g. were used in the experiments. Each group contained six rats distributed equally according to sex and litter mates. The different groups were fed on the experimental diets containing safflower seed oil, niger seed oil, groundnut oil and cow's ghee. The composition of the diet is shown in Table VI. In addition to the diet two drops of Adexoline and 2 mg. of alpha-tocopherol were given orally to each rat, twice a week to meet their vitamin A, D & E requirements. The feeding was carried out for a period of 8 weeks. The average weekly increase in weight as well as the increase in weight per gram of fat intake is given in Table VII. No significant difference was observed between the growth promoting value of safflower seed oil, niger seed oil, groundnut oil and cow's ghee.

TABLE I

Composition of safflower seed and niger seed

Constituent.	Safflower		Niger	
	Whole seed	Kernel	Whole seed	Kernel
Moisture % ...	6·8	6·5	7·8	6·8
Fat %	27·2	46·8	31·3	49·8
Protein (Nx 6·25)% ...	12·53	22·4	19·4	28·1
Ash %	1·68	1·78	1·80	2·80
Calcium %	0·056	0·058	0·05	0·05
Phosphorus % ...	0·25	0·39	0·18	0·26

TABLE II

Characteristics of safflower seed and niger seed oils

Constituent	Safflower seed oil	Niger seed oil
Specific gravity ...	0·921	0·917
Refractive index ...	1·960	1·472
F.F.A. (% oleic) ...	0·45	1·0
Sap. value ...	192·0	188·8
Iodine value ...	130·3	120·5
SCN. value ...	84·0	85·4
Unsaponifiables % ...	0·9	0·6
Saturated acids % ...	6·1	9·2

TABLE III

Glyceride composition of safflower seed and niger seed oils

Fat	Unsaturated	Saturated	Oleic	Linoleic
Safflower seed oil ...	6·4	93·6	36·5	57·1
Niger seed oil	9·5	90·5	37·0	53·5

TABLE IV

Stability of Safflower seed and niger seed oils
(A.O.M. method)

	A.O.M. hours
Crude safflower seed oil	14·5
Refined safflower seed oil	10·5
Refined and bleached safflower seed oil ...	10·0
Crude niger seed oil	11·5
Refined niger seed oil	6·5
Refined and bleached niger seed oil	6·0

TABLE V

Peroxide values of crude, refined and bleached safflower seed and niger seed oils stored at room temp.* (25-30°C) *and* 37°C *at the end of 3 months.*

Fat	Type of container	Peroxide value	
		R.T.	37°C
Crude safflower seed oil	Aluminium ...	62·8	160·2
	Tinned brass ...	68·4	162·0
Refined safflower seed oil	Aluminium ...	90·7	383·8
	Tinned brass ...	111·0	395·6
Refined and bleached safflower seed oil ...	Aluminium ...	166·3	605·6
	Tinned brass ...	182·6	622·8
Crude niger seed oil	Aluminium ...	78·7	188·4
	Tinned brass ...	46·2	79·6
Refined niger seed oil	Aluminium ...	90·6	515·0
	Tinned brass ...	72·6	143·0
Refined and bleached niger seed oil ...	Aluminium ...	186·4	557·5
	Tinned brass ...	85·8	167·2
Groundnut oil	Aluminium ...	16·0	22·0
	Tinned brass ...	14·0	25·0

* Initial peroxide value of the different oils was zero.

TABLE VI

Percentage composition of experimental diet

Casein (fat free) ...	12·0
Corn starch ...	60·0
Sucrose	10·0
Vitaminized starch† ...	4·0
McCollum & Davis salt mixture...	4·0
Fat*	10·0

† Four per cent of vitaminized starch in the diet supplied the daily requirement of all B-group of vitamins.

* The oil or fat included one of the following: Safflower seed oil, niger seed oil, groundnut oil and cow's ghee.

TABLE VII

Comparative rates of growth of rats fed on diets containing different fats

Fat fed*	Average increase in weight per week (g)		Increase in weight per g. of fat intake (g)	
Safflower seed oil ...	12.50	±0·76 (16 d.f.)	1·976	±0·056 (16 d.f.)
Niger seed oil ...	11·85		1·856	
Groundnut oil ...	12·76		2·004	
Cow's ghee ...	12·96		2·06	

* Level of fat in the diet was 10% in all the cases.

TABLE VIII

Digestibility of safflower seed and niger seed oils.

Fat fed	Coefficient of digestibility (%)
Safflower seed oil	98·7
Niger seed oil	95·6
Groundnut oil	98·0
Cow's ghee	98·8

TABLE IX

Effect of safflower seed and niger seed oil on nitrogen, calcium and phosphorus metabolism.

Fat fed	Nitrogen retained %	Calcium retained %	Phosphorus retained %
Nil (fat free diet) ...	49·2	46·8	55·6
Safflower seed oil ...	51·1	60·1	67·1
Groundnut oil ...	50·8	57·2	62·5
Niger seed oil ...	51·9	62·0	66·5
Cow's ghee ...	50·3	55·6	57·6

Digestibility of safflower seed and niger seed oils :

The *in vitro* digestibility of crude safflower seed and niger seed oils was studied using castor seed and pancreatic lipases (Ahmed and Sareen, 1945-46 ; Weinstein, and Wynne, 1935-36). The course of hydrolysis of safflower seed and niger seed oils was nearly the same as those of other edible oils like groundnut oil.

The digestibility coefficients of safflower seed and niger seed oils was determined on adult rats by feeding diets containing the different fats at 10 per cent level. The method adopted was similar to that of Narayana Rao and De (1951). The composition of the diet was the same as that given in Table VI. Calculation for digestibility coefficients were made in the usual manner after correction for metabolic fat. The results presented in Table VIII show that all fats tested are almost completely digestible by rats.

Effect of safflower seed oil and nigerseed oil on nitrogen, calcium and phosphorus metabolism in young rats.

The effect of safflower seed and niger seed oil on nitrogen, calcium and phosphorus metabolism in young rats was determined by the metabolism study (Narayana Rao and De 1952). Rats weighing about 40 g. were fed on an adequate diet (Table VI). During the collection period the rats were kept in individual metabolism cages with arrangements for the collection of urine and faeces. After a preliminary period of 7 days on the experimental diet, the faeces and urine were collected for 7 days and analysed for nitrogen, calcium and phosphorus. From the amount of nitrogen, calcium and phosphorus retained in the body, the effect of different oils on nitrogen, calcium and phosphorus utilization was determined. The results are given in Table IX.

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EFFECT OF DIETARY FATS AND CHOLESTEROL ON THE SERUM POLY-UNSATURATED FATTY ACIDS IN RATS

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Abstract

(i) Increase in body weights of rats was proportional to increasing level of polyunsaturated fatty acids in the diet.

(ii) Average final weights of rats fed with dietary fats and cholesterol seemed to be higher than those fed without cholesterol.

(iii) Total fatty acids in serum of rats maintained on dietary fats with cholesterol were more in percentage than those without cholesterol, with the influence of cholesterol added to diets. The level of individual fatty acids expressed as a percentage of total fatty acids was lowered gradually, except the level of trienoic acid.

Introduction

The recent interest in the possible role of unsaturated fatty acids in the regulation of serum cholesterol levels has stimulated a great deal of research to determine a relationship between essential fatty acids and cholesterol metabolism. The inter-relationship between the metabolism of the highly unsaturated fatty acids and that of cholesterol was first suggested by Bloor. After examining the blood of sheep, cow, pig and dog Bloor (1923) noted that the fatty acids in combination with cholesterol have the highest iodine number of those in any fraction. Also, the influence of cholesterol in transporting essential fatty acids has been suggested by Kelsey and Longenecker (1941) and by Alfin-Slayter *et al.* (1954). It was observed in rats by Pifer and Holman (1955) that the dietary cholesterol and physiological stresses which induced hypercholesterolemia accelerated development of essential fatty acids deficiency. This paper is a report on the composition of polyunsaturated fatty acids in the blood serum of rats maintained on twenty per cent dietary fat with or without cholesterol for nearly ten months. This work was undertaken to see the relationship between the growth of rats and poly-unsaturated fatty acids present in the diet and also to observe the influence of feeding cholesterol on the growth and serum polyunsaturated fatty acids in rats.

Methods

Young male albino rats, 4 weeks old and weighing between 35 to 50 g. were distributed into four groups. Each group of rats was fed for the first week with a fat free diet. Afterwards, they were maintained on diets which contained either 20 per cent of coconut oil, Dalda, ghee or groundnut oil. The other ingredients of the diet were 22 per cent casein, 4 per cent salt mixture (Hawk and Oser, 1931) and 54 per cent sucrose. The rats were given all the required vitamins in sufficient quantities (Panos and Finerty, 1954). After six weeks on the control diet, the first eight rats of each group were given 0·5 g. of cholesterol per kilogram of the body weight of the

rat. The remaining six were maintained on 20 per cent fat as controls. Rats were weighed twice a week and their daily food intake and growth recorded. The cholesterol was mixed in the respective oils and the oils and then mixed with the diets. At intervals, some rats were sacrificed under ethyl ether anesthesia. Fasting blood samples were drawn by heart puncture, using sodium citrate as an anticoagulent.

Preparation of fatty acids

3 ml. of serum were added to 20 ml. of 3:1 alcohol-ether mixture. The extract was heated to boiling and then filtered. Two additional hot extractions of the protein residue were made. To the total filtrate 0·2 ml. of 0·1 per cent alcoholic hydroquinone and 0·1 ml. of 50 per cent KOH were added. The extract was evaporated nearly to dryness on the water bath for about 45 minutes. After saponification, 5 ml. of water were added to dissolve the soaps and the fatty acids were precipitated with 5 per cent HCl. The petroleum ether (40-60°C. b.p.) was added and the flasks were kept overnight. Then the petroleum ether layer was carefully separated and again 0·1 per cent hydroquinone was added to those extracts. The extract was evaporated to about 3 ml. The fatty acids were resaponified at room temperature with 3 m. of 0·1 N alcoholic KOH (freshly prepared) and 3 ml. of distilled water by emulsifying thoroughly. After standing for one hour the tubes were centrifuged to ensure complete separation. The upper layer of unsaponifiables was discarded. The solution of the soaps was evaporated nearly to dryness. This required for 2 to 2½ hours, 5 ml. of distilled water were added and the fatty acids were precipitated with 5 per cent HCl. The fatty acids dissolved in petroleum ether were washed and purified. The fatty acids were dried under vacuum to constant weight and analysed spectrophotometrically by the method of Herb and Riemenschneider (1953). Calculations for the percentage of the individual polyunsaturated fatty acids were made according to Herb and Riemenschneider, as modified by Hammond and Lundberg (1953) for the inclusion of hexaenoic acid. In the formulae used in the present work, the assumption was made that the pentaenoic acids consist of 50 per cent docosapentaenoic and 50 per cent eicosapentaenoic acids.

Results and Discussion

In this experiment, the dietary fats used were very fresh and their peroxide value was negligible. The iodine values and composition of polyenoic acids of coconut oil, butter fat (ghee), hydrogenated fat (Dalda), and groundnut oil were as follows:—The iodine values were 9·7, 33·2, 66·0 and 91·0, respectively. The percentages of linoleic acids were 2·0, 1·7, 0·3 and 26·2 respectively. Other polyenoic acids were present in traces. The casein used contained 1·5 per cent of linoleic acid. Other polyenoic acids were present in small quantities (1 per cent).

The average increase in body weight of rats maintained on twenty per cent dietary fats with or without cholesterol is given in Table I. The influence of feeding cholesterol on the growth of the rats is rather significant.

TABLE I

The average increase in body weights of rats in g., per month fed on dietary fats with and without cholesterol.

Group No. ...	I	IA	II	IIA	III	IIIA	IV	IVA
No. of rats at start ...	6	8	6	8	6	8	6	8
Dietary fats* ...	Coconut oil 20%	Coconut oil 20% + cholesterol	Dalda 20%	20% + cholesterol	Ghee 20%	Ghee 20% + cholesterol	Groundnut 20%	Groundnut 20% cholesterol
Mean initial weight g.	36	40	35	42	34	40	36	42
No. of months								
1	44	50	46	41	54	58	63	61
2	40	62	43	65	44	65	33	64
3	40	43	43	32	42	39	45	40
4	27	14	40	18	22	24	37	23
5†	14	20	15	27	14	17	27	30
6	10	9	15	17	8	21	23	19
7	15	−1	13	20	15	7	12	20
8	−3	10	03	12	10	8	10	8
9	12	7	5	0	6	2	5	5
10	2	2	2	4	3	1	4	6
Final weight of rats ...	237	256	260	278	252	283	295	318

* 0·5 g. of cholesterol per kilogram weight of the rat is fed after six weeks.
† After 19 weeks three rats from each group were killed.

TABLE II

Polyunsaturated fatty acids in serum of rats.

Group No.	Dietary fats and cholesterol	Cholesterol feeding period in weeks	Individual Polyenoic fatty acids					Total fatty acids in mg. per 100 c.c. of serum
			Dienoic	Trienoic	Tetraenoic	Pentaenoic	Hexaenoic	
I	Coconut oil 20% ...		10·1	2·3	10·2	0·42	0·61	610
Ia	Coconut oil 20% + cholesterol ...	34	7·29	3·0	6·0	0·31	0·51	722
II			11·12	1·0	12·3	0·77	1·05	492
IIa	Dalda 20% + cholesterol ...	34	9·8	1·01	10·1	0·52	0·81	540
III	Butter fat 20% ...		12·3	1·1	10·2	0·80	0·82	520
IIIa	Butter fat 20% + cholesterol ...	34	9·64	1·2	7·0	0·65	0·71	610
IV	Groundnut oil 20% ...		20·4	0·61	18·4	1·1	1·24	610
IVa	Groundnut oil 20% + cholesterol ..	34	19·1	0·45	13·0	1·0	1·1	625

The average final weight of the rats maintained on four groups of fats with cholesterol seemed to be higher than those without cholesterol. From Table I, it was observed that in all groups the increase in body weight of rats was directly proportional to the increasing amounts of essential fatty acids in the diet. This was already observed by Greenberg *et al.* (1950).

Polyunsaturated fatty acids in serum of rats are noted in the Table II. Effect of feeding different fats changed the distribution of polyenoic fatty-acids in the serum. In the first three groups maintained on coconut oil, Dalda and ghee the percentage of linoleic acid was low as compared to the percentage of that in the groundnut oil group. This was due to the higher percentage of polyenoic fatty acids in the diet of group IV. In the first group, the trienoic acid was 2·3 per cent ; in others groups it was very insignificant, the tetraenoic acids in groups I, II and III varied from 10·2 to 12·3 per cent. The tetraenoic acids were predominantly present (18·4 per cent) in the group IV. Pentaenoic and hexaenoic acids were present in traces in all groups. Both these acids may also be derived from linoleic acid.

Addition of cholesterol to diets seems to change the distribution of polyenoic fatty acids in serum. In groups Ia, II, IIIa the level of linoleic and tetraenoic acids was lowered gradually. In group IVa the percentage of linoleic acids was not much altered, but the level of tetraenoic acids was markedly lowered. This might be the result of an increased catabolism of this acid and because of the presence of a higher amount of cholesterol deposition. The percentage of trienoic acid in group Ia was increased from 2·3 to 3 per cent. Both the pentaenoic and hexaenoic acids appeared to be lower in all groups. The percentage of total fatty acids in control groups seemed to be lower than that of cholesterol fed groups.

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STUDIES ON THE BIO-ISOMERISATION OF INGESTED FATS

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It has recently been observed that seed fats of the Cucurbitaceae family, obtained from common vegetables, usually consumed by people all over India contain substantial amount of conjugated triene acids (α-elaeostearic acid). Thus the familiar *parwal* (Tricosanthes diocia), Karela (M. charantia), and snake gourd (T. anguina) contain between 30-50 per cent of α-elaeostearic acids in conjunction with linoleic, oleic and other saturated acids. Some other seed fats of the same family again e.g. gourd (C. maxima), bottle gourd (L. vulgaris) etc. contain non-conjugated acids like linoleic, oleic and saturated acids. It is well known that depot fats of animals do not contain any conjugated acid. The aim of the present work is to follow the course of isomerisation of the conjugated fatty acids to non-conjugated ones, given as a dietary fat to animals. As stated above, many studies have been made on the subject of preformed fats by animals, but very little on the bioisomerisation appears to have been made. The reason, perhaps, is that normally the dietary fats used in most countries do not contain conjugated fatty acids. The dietary preformed fats are dealt not in the liver but in the epithelial cells of the small intestines and finally emerge into the blood stream, a peculiarity which has rendered the ingested fat more amenable to experimental study. In as much as, the presence of conjugated fatty acids in some of the Cucurbitaceae seed fats lend themselves to easy detection by spectrophotometric procedure, it was expected that the interference with the normal composition of animal-depot fats as a result of ingestion would be followed quite easily.

Experimental

Two sets of animal experiments with rats were started, each being divided into two groups—control and experimental. The animals were maintained in separate cages with proper identification, on a fat-free diet for a period of seven days. In one set, the rats were maintained on a diet of 10 per cent fat level (supplemented with all other essential accessory food factors), which being refined M. Charantia fat for the experimental groups and refined groundnut oil for the control group, for a period of two weeks and in the other set the rats were maintained on the above diet for five weeks. After the required period the animals were killed, the carcass isolated from the other organs like brain, liver etc., and the fat extracted according to standard method (Kaplan, 1935) with alcohol-ether mixture and finally with ether.

The various analytical characteristics of the body lipids have been determined and the percentage conjugated trience acid calculated by following the

spectrophotometric method (Hilditch, Morton and Riley, 1945: Patel and Riley 1951). The Percentages of linoleic and linoleic acids present in the body fat of rats belonging to both the groups have been determined by the spectrophotometric method after alkali isomerisation at 180°C for 60 mins. and 170°C for 15 min. respectively. The growth promotion and feed efficiency for a period of six weeks have also been worked out.

The analytical figures and composition of the two dietary fats (control and experimental) are as follows:—

Table I

		M. charantia oil		G.N.O.
Sap. Equivalent	...	293·6		293·0
I.V. (Wij's)	...	140·0		96·0
		Percentage fatty acid composition		
Conj. trience	...	43·0		Nil
Lionleic	...	12·5		27·5
Satd. (Bertran's	...	12·5		55·0
Oleic by diff.)	...	32·0	(Satd. by diff.)	17·5

Table II

Growth promotion and feed efficiency.

Group	Avg. initial body wt. gms.	Avg. final body wt. gms.	Avg. gain body wt. gms.	Total food consumed Avg. gms.	Gain/gm. of food	Gain/Cal.
Control	24	124	100	335	0·299	0·0638
Exptl.	24	100·5	76·5	335	0·228	0·0486

I Set.

Control and experimental diet with 10 per cent fat level (supplied with all accessory food factors) continued for two weeks. The carcass lipids of two to three rats in a group were pooled, and their lipids were analysed together for convenience.

Table III

Control group (G.N.O. as fatty constituent)

Rat Nos.	Body fat		Analysis of mixed fatty acids of body fat		
	I.V.	S.V.	% α-Elaeostearic	% Linolenic	% Linoleic
1, 2	60·7	187·5	0·25	1·5	13·5
3, 4	62·3	189·0	0·20	1·2	14·1
5, 6, 7	64·1	190·3	0·21	1·7	13·8

Table IV

Experimental (M. charantia as fatty constituent).

Rat Nos.	Body fat		Analysis of mixed fatty acids of body fat		
	I.V.	S.V.	% α-Elaeostearic	% Linolenic	% Linoleic
8, 9	66·2	187·6	0·23	5·4	4·8
10, 11	68·5	191·8	0·20	5·7	4·9
12, 13, 14	70·6	189·5	0·18	6·4	4·6

II Set

Control and experimental diet with 10 per cent fat level (supplied with all other essential accessory food factors) continued for *five* weeks. In each group two or three rats were pooled and the lipids were analysed together for convenience.

TABLE V

Control (Groundnut oil as fatty constituent).

Rat Nos.	Body fat		Analysis of mixed fatty acids of body fat		
	I.V.	S.V.	% α-Elaeostearic	% Linolenic	% Linoleic
15, 16	68·0	186·5	0·38	1·7	16·2
17, 18	65·0	192·3	0·25	1·5	15·9
19, 20, 21	70·5	194·5	0·37	2·0	15·4

TABLE VI

(M. charantia fat as fatty constituents).

Rat Nos.	Body fat		Analysis of mixed fatty acids of body fat		
	I.V.	S.V.	% α-Elaeostearic	% Linolenic	% Linoleic
22, 23	74·0	194·3	0·28	7·9	3·5
24, 25	78·5	192·0	0·19	8·9	3·6
26, 27, 28	73·3	187·5	0·15	7·5	3·0

Discussion and Conclusion

During the course of the experiment it was observed that the rats of the experimental group excreted greater quantities of stool of semi-solid consistency and whitish in colour, indicative of a diarrohœic nature. The rats of the control groups were of bigger size, but otherwise the conditions of the experimental rats were normal. At the time of dissection it was found that the condition of the individual organs were normal in both the groups except that they were slightly smaller in size in the experimental group.

It is seen from the above results that in all the cases of the experimental groups there is very little deposition, if at all, of conjugated acids as such contained in the ingested fat. It is also interesting to observe that the body fats of the experimental rats contain an appreciably higher percentage of linolenic acid thereby indicating that a portion of the ingested elaeostearic acid may have been isomerised to its non-conjugated form. Of course the small amount of linolenic acid in the control group fat shows the possibility of formation of this acid from linoleic acid present both in the experimental M. Charantia fat and the control ground oil. The difference in the linoleic acid content of the depot fat of the control and experimental groups is quite appreciable and may be due to the difference in composition (i.e. the difference of linoleic acid content of the dietary fats) of groundnut oil and M. charantia fat. As stated before the linoleic acid content of depot fats is almost wholly influenced by the dietary fat.

Further work regarding the fate of the ingested elaeostearic acid, whether it be oxidized or broken down and re-synthesised, is in progress. More complete analysis of the depot fats with regard to the other unsaturated acids like arachidonic is also being carried out.

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SECTION F

CHEMISTRY OF FATS AND OILS

MODE OF FRACTIONATION OF CHAULMOOGRA OIL FATTY ACIDS WITH UREA

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Abstract

The fatty acids of chaulmoogra oil were fractionated with urea to study the mode of separation. Aliphatic acids separate first and are followed by chaulmoogric, hydnocarpic, alepric, aleprylic, and gorlic acids. The lower homologues of hydnocarpic acid and gorlic acid do not form stable adduct with urea at room temperature (30°C).

Chaulmoogra oil from seeds of some species of the family *Flacourtiaceae* has been used for many centuries in treatment of leprosy. But it was not until 1904-7 that Power and his associates (Power and Gornall, 1904 ; Power and Barrowcliff, 1905, 1907*a*, *b*) reported their investigations on the constituent chaulmoogric and hydnocarpic acids, although these were sometimes erroneous in regard to the actual structures. It has been conclusively proved around 1920 that these cyclic acids are responsible for their curative properties (Muir, 1919, 1920 ; Walker and Sweeney, 1920 ; Schobl, 1923).

Hydnocarpic acid was originally obtained by Power and Barrowcliff (1905) from the *Hydnocarpus wightiana* and other oils by fractional crystallisation of the barium salts of their fatty acids. Brill (1916, 1917) and Brill and Williams (1917) confirmed this work by isolating chaulmoogric and hydnocarpic acids and recrystallised hydnocarpic acid from the lower boiling fraction. Gorlic acid was detected and later isolated by Andre and Jouatte (1928*a*, *b*). Many subsequent attempts have been made (Stacks and Adams, 1926 ; Perkins *et al.*, 1927 ; Paget, 1937) to isolate the fatty constituents by various methods.

Systematic study of the proportions of the components of the oil was undertaken by Cole and Cardoso. After first determining the analytical constants for the pure acids and their ethyl esters (Cole and Cardoso, 1937), the composition of different oils was determined by preliminary separation of the fatty acids by low temperature crystallisation followed by fractional vacuum distillation (Cole and Cardoso, 1938). The major components of chaulmoogra oil are chaulmoogric, hydnocarpic and gorlic acids which together comprise about 80 per cent of the total. Along with some oleic, palmitic and stearic acids are also present in minor proportions. The structure of the four optically active cyclic acids and their analytical characteristics (Cole and Cardoso, 1939) are given in Table I.

It is now well known that urea separates organic compounds according to unsaturation, chainlength and branching. The branching present in an aliphatic chain tends to restrict the formation of a complex with urea. The dimensions of the urea channel given by Swern and co-workers (1952) are 5·5. to 6·0 A.U. The formation of complex is not possible if the dimensions

of the branching are more. But if there is a branching or a cyclic ring at the end of an aliphatic chain the formation of the complex depends on its chain-length and unsaturation. Schlenk (1949) observed that although benzene itself does not form complex with urea, the long aliphatic chain of octadecylbenzene provides enough energy to include the molecule in the channel. The cyclic acids of chaulmoogra oil have a cyclopentene ring attached to aliphatic side chains of different lengths and unsaturation. Their mode of separation with urea has been studied in the present work.

Experimental

The chaulmoogra oil, obtained locally, was of the *Hydnocarpus Kurzii, King* group and had the following characteristics S. V. 201·1, I. V. (Wijs) 98·1, F. F. A. 2·25 per cent, unsaponifiable matter 0·4 per cent and specific optical rotation + 54·35°. These are similar to the reported values (Brill, 1916 : Cole and Cardoso, 1937).

Fractionation of the mixed fatty acids with urea :

The mixed fatty acids (50g., I. V. 100·5, N. V. 207·7, specific rotation, ($[\alpha]_D$ + 57·97°) of the chaulmoogra oil, prepared as usual (Hilditch, 1949). were dissolved in absolute ethyl alcohol (500 ml.) and urea (60 g.) was added. The mixture was warmed on water-bath, left overnight, and filtered through a sintered glass funnel. The adduct obtained was decomposed by warm acidulated distilled water and the fatty acids isolated, using ether. Further fractions were obtained by successive addition of urea to the raffinates and removal of the adducts formed. The various fractions were analysed for iodine and neutralisation values and specific optical rotation in sodium light $[\alpha]_D$ in chloroform solvent. Results are included in Table II.

Discussion

The iodine and neutralization values and specific optical rotations of fractions show that the separation of chaulmoogra fatty acids with urea follows a definite trend. The iodine value rises with every fraction while the neutralization value and specific optical rotation, which are related to the molecular weight, rise in the beginning, fall in the fourth fraction and finally rise in the fifth. This shows that urea separates these acids on the basis of chainlength and unsaturation similar to the normal straight chain acids. The specific optical rotation of the first two fractions is less than 60·3° which is the least exhibited by any of the cyclic acids of chaulmoogra oil (Cole and Cardoso, 1939) indicating the presence of aliphatic acids in these fractions.

As reported by Cole and Cardoso (1939, p. 2351), the important acids of chaulmoogra oil are chaulmoogric, hydnocarpic, alepric, aleprylic and gorlic which contain a cyclopentene ring attached to carbon chain lengths of 13, 11, 9, 7 and 13 respectively, gorlic-acid having a double bond in the side chain.As the separation of these acids is based on the chainlength and unsaturation of the side chain, the order in which the acids with saturated side chain would appear is chaulmoogric, hydnocarpic, alepric and aleprylic.

Gorlic acid would come in later fractions. During urea fractionation (Mehta *et al.*, 1956) oleic and saturated C_{18} acids have the same adduct forming tendencies. The presence of one double bond reduces the effective chain-length of an acid by about five carbon atoms so far as adduct formation is concerned. If this phenomenon also takes place with the cyclic acids with side chains, gorlic acid would appear with alepric acid which has a saturated C_9 side chain.

These arguments as well as consideration of analytical characteristics of fractions and pure acids (Cole and Cardoso, 1939, p. 3442) lead to the mode of fractionation of chaulmoogra acids with urea. The fractions are binary or ternary mixtures. In the first fraction aliphatic acids accompany chaulmoogric acid. Second and third fractions are mixtures of chaulmoogric and hydnocarpic acids with a little quantity of aliphatic acids. The proportion of these acids decreases in the fourth fraction. The fifth fraction contains gorlic acid together with lower homologues of hydnocarpic acid. To confirm this mode of fractionation approximate composition of each fraction was calculated from its iodine and neutralization values and specific optical rotation according to the method of Cole and Cardoso (1938, p. 614) A sample calculation is given below.

Fraction I. 6·36g., I. V. 94·4, Sp. rot. +42·74°, N.V. 201·4. Chaulmoogric acid calculated from specific rotation; allowing for I. V. of chaulmoogric acid, I. V. of remainder was calculated and oleic acid determined; from N. V. of components and mixture, N. V. of saturated acid portion calculated and partitioned between palmitic and stearic acids. Fraction 2. 16·22g. I. V. 98·8, Sp. rot. 55·75°, N. V. 204·9. Calculated to chaulmoogric, hydnocarpic, oleic and palmitic acids using these analytical characteristics and four simultaneous equations. Calculations for fractions 3, 4 and 5 are similar to those for fraction 2. The results (Table II) are comparable to those of Cole and Cardoso (Table III). This confirms the mode of fractionation outlined above and indicates the possibility of separation of cyclic acids of chaulmoogra oil with urea.

TABLE I

Structures and analytical characteristics of cyclic fatty acids present in chaulmoogra oil (Cole, *et al.* 1939).

Acid	Structure	Mol. wt.	N. V.	$[\alpha]_D$ +	I.V.
Chaulmoogric	$\begin{matrix}CH=CH\\ \vert \quad > CH(CH_2)_{12}CO_2H\\ CH_2—CH_2\end{matrix}$	280·2	200·2	60·3	90·5
Hydnocarpic	$\begin{matrix}CH=CH\\ \vert \quad > CH(CH_2)_{10}CO_2H\\ CH_2—CH_2\end{matrix}$	252·2	222·5	69·3	100·7
Aleprylic	$\begin{matrix}CH=CH\\ \vert \quad > CH(CH_2)_6CO_2H\\ CH_2—CH_2\end{matrix}$	196·2	286·0	90·3	129·7
Gorlic	$\begin{matrix}CH=CH\\ \vert \quad > CH(CH_2)_6CH=CH(CH_2)_4CO_2H\\ CH_2—CH_2\end{matrix}$	278·2	201·7	60·7	182·5

TABLE II

Fractionation of the mixed fatty acids of chaulmoogra oil by stepwise addition of urea.

Fatty acids taken 50g. N.V. 207·7, I.V. 100·5, Specific Optical Rotation 57·97°.

Fraction No.	...	1.	2.	3.	4.	5.	
Urea added (g.)	...	60	50	50	75	Raffinate	Total.
Wt. of fraction (g.)	...	6·36	16·22	13·89	0·92	10·85	—
I.V.	...	74·4	90·8	98·9	116·1	135·2	48·24
N.V.	...	201·4	204·9	210·3	200·3	208·3	—
Specific rotation (Degrees)	...	42·74	57·75	61·20	61·0	63·0	—
							—
Approximate composition (g) : Acid							
Chaulmoogric	...	4·51	1·08	6·77	0·60	—	12·96
Hydnocarpic	...	—	12·12	6·38	0·06	—	18·56
Aleprylic	...	—	—	—	—	0·83	0·83
Gorlic	...	—	—	—	0·26	10·02	10·28
Oleic	...	0·72	1·73	0·74	—	—	3·10
Palmitic	...	0·51	1·29	—	—	—	1·80
Stearic	...	0·62	—	—	—	—	0·62

TABLE III

Fatty acids composition of chaulmoogra oil (Hydnocarpus Kurzii).

Acids		Cole and Cardoso (1939) %	Present work %
Hydnocarpic	...	34·9	37·12
Chaulmoogric	...	22·5	25·92
Gorlic	...	22·6	20·56
Lower homologues of hydnocarpic	...	0·4	1·66
Oleic	...	14·6	6·38
Palmitic	...	4·0	3·60
Stearic	...	—	1·24
Loss	...	1·0	3·52

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BODYING OF LINSEED OIL

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The importance of drying oils as materials for protective and decorative coatings is due to their ability to form plastic films. Their film-forming properties are closely related to their degree of unsaturation and the position of unsaturated bonds. These unsaturated groups are the active centres of polymerisation and/or oxidation. In case of polymerisation, ether elevated temperature or catalyst is necessary. On the other hand oxidation may take place at room temperature or even at lower than that. Both the processes namely polymerisation and oxidation, quicken the time of film formation. So in industry either polymerised and/or oxidised oils are largely used.

The methods of manufacture hitherto known as batch processes, are time-consuming. The thermal efficiency of the known methods is not high. Since heat transfer in a bad conductor like oil is a difficult task, more so when it is thickened and uniform heating is never attained by the known methods.

It was therefore thought worthwhile to find out a method of manufacture of polymerised and/or oxidised oil, which would require less time and would have a higher thermal efficiency than the common methods known.

Experimental :

The apparatus is a U-tube of which one arm is short and wide while the other arm is very long and narrow. At the base of the U-tube, there is a stop-cock to control the rate of flow of liquids from one arm to the other.

An eutectic salt mixture consisting of 53 per cent KNO_3, 7 per cent $NaNO_3$, 40 per cent $NaNO_2$ by weight was taken in the wider arm and the salt mixture was melted by heating electrically. Samples were taken in the narrow arm, when the stop cock was opened, due to hydrostatic pressure the oil passed through the heated salt mixture and collected at the top of the wider arm and came down the overflow pipe. Prior to passing the oil through the molten salt, dry CO_2 gas was passed to drive out all air from the salt. The treated oils were allowed to stand in closed vessels. They were found to separate in two layers within a few minutes. The upper layer was a liquid and the lower one was semi-solid. They were separated by centrifugation. at 3500 r.p.m. for half an hour.

Table

Bath temperature	310°C
Exit temperature	205°C
Flow rate	25 c.c./minute
Acetone Solubility of treated linseed oil	89·5%
Ether Solubility of same	89·0%
Aldehydes and Ketones	7·07%

	Original oil	Acetone Soluble fraction	Acetone insoluble fraction
Ref. Ind.	1·4740	1·4745	1·4760
Mol. Wt.	875	895	1548
Acid value	0·76	0·89	3·2
Iodine value	180·8	178·0	134·0
Peroxide value	0·1	14·6	2296
Acetyl value	0·1	32·5	47·8

Peroxide value has been expressed as milliequivalents of oxygen per 1000 gram of fat.
% Nitrous acid before experiment in the Eutectic mixture 27·75.
% Nitrous acid after experiment in the eutectic mixture 33·81.

Discussion.—The table shows that about 10 per cent of the treated linseed oil is insoluble in acetone which indicates that not only oxidation but certain amount of polymerization has also taken place. The figures for aldelydes and ketones point out that certain amount of break down of the molecules has taken place. The break down may take place at two places, either at the double bonds and/or at the esterlinkages. No sign of acrolein evolution was observed which supports the view that the breakdown took place at the double bonds. Besides forming olefine hydroperoxides, it is also believed that a small proportion of oxygen adds on to the double bonds to give cyclic moloxide which then undergoes scission at the c-c-bond to give two molecules of an aldelyde or ketone e.g.

$$-CH = CH- + O_2 \rightarrow \underset{\underset{O-O}{|\quad|}}{-CH-CH-} \rightarrow -CHO + OHC-$$

The consistency of the treated oil was found to be highly viscous, but on standing. It separated in two layers. This presented a new problem since in the preparation of bodied oils by the methods hitherto known no separation does take place.

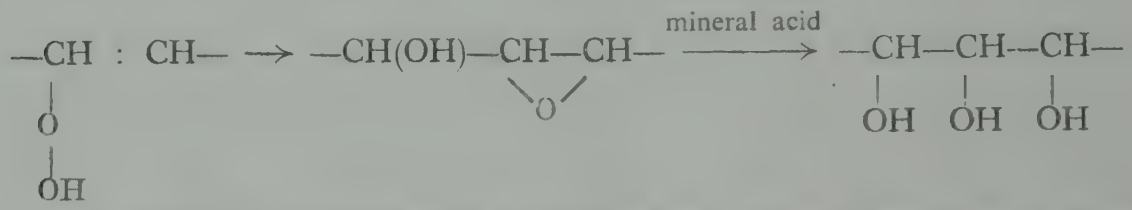
From the table it is found that one fraction is soluble in acetone and the other fraction insoluble. In the case of polymerized oils prepared by known methods the acetone insoluble fraction remain in solution in the so-called monomer. The separation in the present case may be due to following reasons :—

(*i*) The polymerized molecules do not find enough time to orient themselves in such a fashion as to enmesh the so-called monomer left after reaction.

(*ii*) Secondly, it may be that due to the presence of hydroxyl groups hydrogen bonding takes place which allows a physical aggregate to form. In that case it should have been soluble in acetone but there are cases where hydrogen bonding makes such physical aggregates insoluble in solvents wherein the monomers are freely soluble.

(*iii*) Thirdly, it may be due to the simultaneous oxidation and polymerization, that a newer type of molecules has been formed which are not soluble in monomer or in acetone or ethyl ether.

The physical and chemical properties of the acetone soluble fraction have been found to be altered as is evidenced from the data in the table. The mol. Wt. is almost the same with that of the original oil. The chemical properties have been changed to a considerable degree. Most significant is the acetyl value which has been increased by 32 units. The increase in acetyl value may be due to the hydrolysis of the fats or due to the formation of hydroxyl groups by the oxidation of the fat itself. Slight increase in the acid value does not support the former view. Therefore, it is more likely that the Glyceride itself has been oxidised. According to Farmer (1942), hyroxyl groups may be formed by the following mechanism:



The peroxide value has been increased by 14 units. Although, it is not much, it points out that both hydroxylation and peroxidation are taking place. Now it remains to be seen which is the precursor of the other or whether they are independently formed of one another. The decrease in iodine value is only by 2 units. This accounts for the formation of hydroxyl groups which have shown by the rise of acetyl value. The decrease in double bonds may support the formation of peroxides according to the mechanism given above.

The acetone insoluble fraction has got acid value which is larger than that of the original oil or of acetone soluble fraction. The high acid value of this sludge which is insoluble in acetone gives an indication that the carboxyl group is attached to the glyceride molecule which is insoluble in acetone. This is another problem which has never been observed i.e. not found in the processed oils by the ordinary methods. The acid present in the oils processed by ordinary methods cannot be separated by centrifugation. The diminution in I. V. by about 50 units can support the formation of such a large amount of peroxide.

Acetyl value has been increased by 47 units. In this case it can be explained that the hydroxyl groups have been formed at the cost of unsaturation. The increase in Mol. Wt. shows that polymerization has taken place. The whole work was done in the atmosphere of dry carbondioxide, naturally then the oxygen has been contributed by the salts which are at the higher stages of oxidation. From the results of the table it is found that the nitrite content of the bath has been increased. The increase of the nitrite may be due to decomposition which is not possible at the temperature of this experi-

ment. Hence it must have been increased due to the reduction of nitrates which have oxidised the oils.

As this is a preliminary work and no information is available about the reaction of this eutectic mixture with the fatty oils ; other typical oils, namely, castor and groundnut only have been tried.

In conclusion it may be safely expected that this new process of oil-bodying will open up a new channel for the study of the oil bodying both in theoretical and in industrial aspects. The polymerized portion of oils can be easily separated for their industrial application. The simultaneous polymerization and oxidation is likely to help to get tailored products.

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CONJUGATION CHANGES IN GROUNDNUT OIL

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Abstract

Under a variety of conditions, groundnut oil may give rise to conjugated products. Alkali isomerisation leading to the formation of diene conjugated linoleate is now used as a common analytical technique. When autoxidised, the oil develops peroxides, a part of which is diene conjugated. When such an oil containing peroxides is treated with acidic bleaching clays, the oil develops triene conjugation, the peroxides being eliminated in the process; treatment with reducing agents like potassium iodide and acetic acid also results in the formation of conjugated triene. Oils containing conjugated triene as a consequence of bleaching, when subjected to autoxidation, again exhibit characteristic conjugation changes: as the peroxide value rises, the conjugated triene gradually disappears ultimatelty vanishing completely at rather low peroxide level, and the conjugated diene goes on increasing until peroxides begin to decompose.

Under a variety of conditions, linoleic acid-oils may give rise to conjugated forms; the simplest and the most common is the conjugated diene resulting from alkali isomerisation. During autoxidation, linoleic acid gives rise to diene conjugated hydroperoxides (Farmer, 1943; Gunstone and Hilditch, 1945). In course of bleaching, linoleic acid oils develop triene conjugation which is characteristic of acid activated bleaching clays (Mitchell and Kraybill, 1942; Sen Gupta, 1956). In the present paper, some of these changes have been studied with respect to groundnut oil and an attempt has been made to define more closely the conditions leading to conjugation development.

Experimental

The oil used in these experiments was a peroxide-free groundnut oil, free from unsaponifiables and free fatty acids, purified by passage through chromatographic alumina (Sen Gupta and Basu, 1952). For autoxidation, samples of the oil were exposed to 60°C in an electric oven in small weighing tubes. At different intervals, samples were withdrawn and peroxide value and u. v. absorption spectra determined with a model DU Beckman spectrophotometer. For iodide treatment, 1 g. of oil dissolved in 10 c.c. of chloroform-acetic acid (2:3) was mixed with 1 c.c. of saturated potassium iodide; at the end of one hour, the chloroform layer was thoroughly washed, first with a potassium iodide solution and then water: the solvent was finally evaporated out and the residual oil examined for ultraviolet absorption. The concentration of the oil in all cases of spectrophotometry was 0·025 p.c. in cyclohexane and the cell was of 1 cm. light path length.

Results

The changes in the spectrophotometric absorption spectra and peroxide values consequent on autoxidation are shown in tables A and B and in Figures 1 and 2. The spectrophotometric absorption curves resulting from treatment with potassium iodide + acetic acid, and chlorine treated clay are shown in Figure 3. (Curves 1, 1A and 2, 2A respectively).

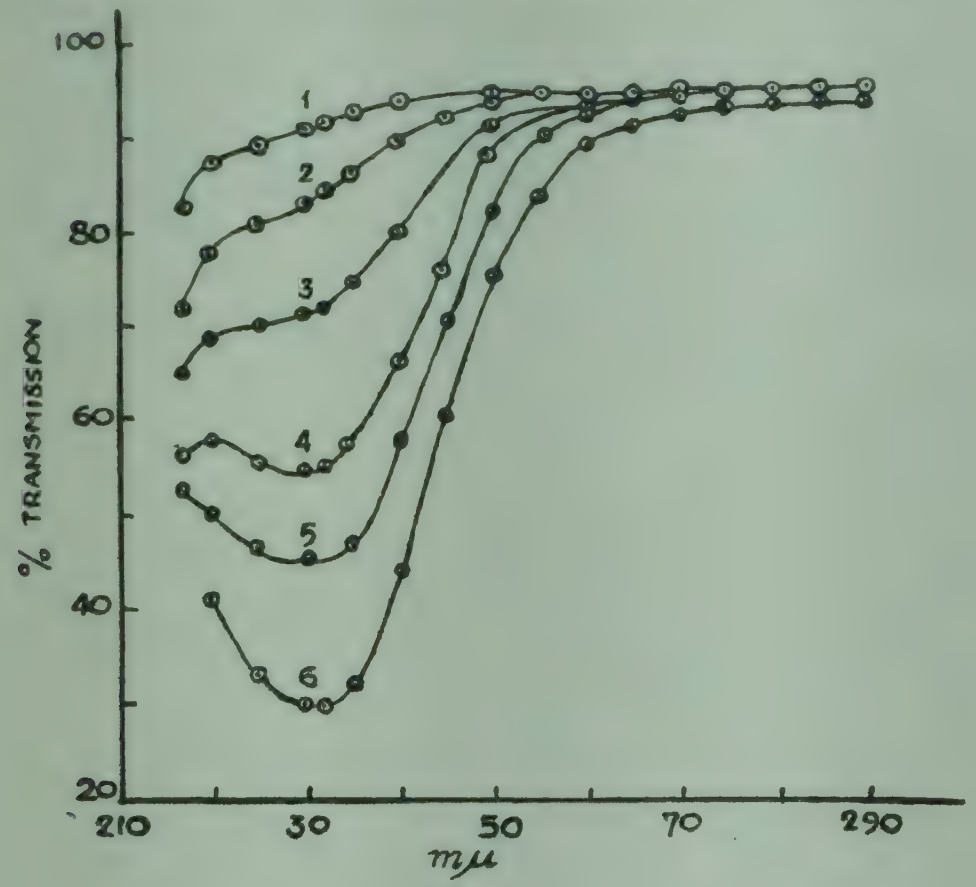
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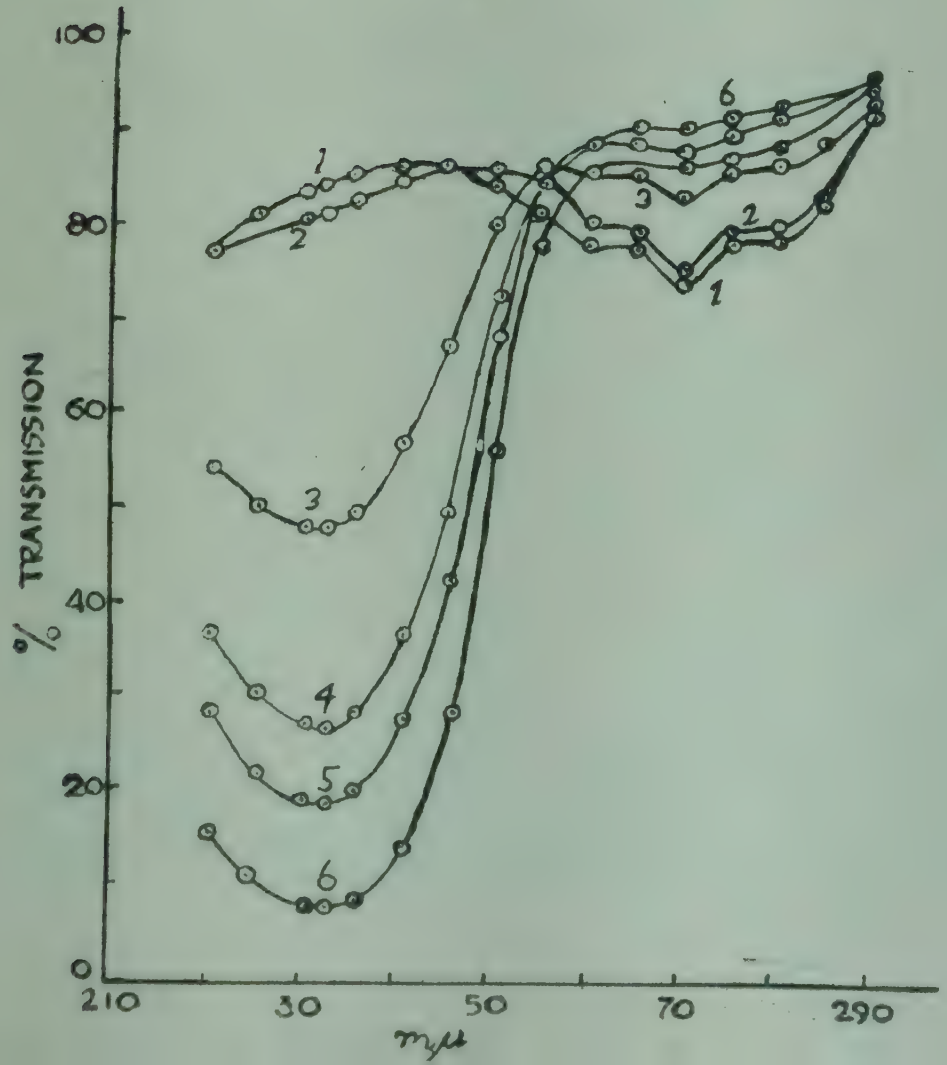
Fig. 1.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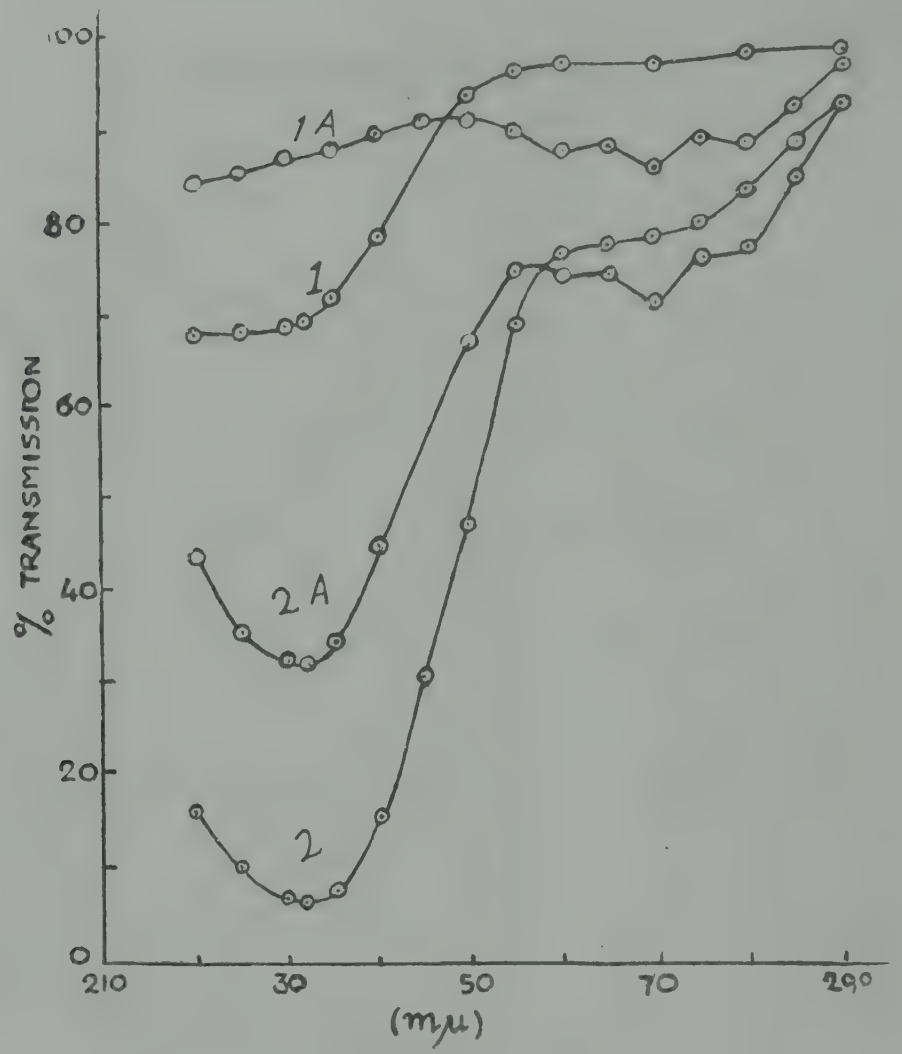

Fig. 3.

TABLE A

Autoxidation and conjugation development (oil initially free from conjugation)

Sample No.	Period of autoxidation (Hours).	Peroxide value.	$E^{1\ p.c.}_{1\ c.m.}$ at 232 mμ	$E^{1\ p.c.}_{1\ c.m.}$ at 270 mμ
A 1	0	0	1·41	0·66
A 2	2	7·5	2·82	0·73
A 3	4	9·8	3·4	0·78
A 4	6	11·4	4·18	0·82
A 5	9	24·4	5·49	0·87
A 6	12	39·8	10·13	0·87
A 7	14	72·9	13·36	0·95
A 8	16	67·0	13·3	0·71
A 9	19·75	128	19·8	0·95
A 10	23	130	20·74	0·95

The starting oil referred to in Table A is one from which peroxides, unsaponifiables etc. were eliminated by adsorption on alumina (loc. cit). This oil, when autoxidised and then treated with filtrol, an acid-treated clay, gives rise to the triene conjugated peroxide free oil, represented by sample B 1 of the following Table B.

TABLE B

Autoxidation and Conjugation Development (Oil initially containing conjugated triene).

Sample No.	Period of autoxidation (Hours).	Peroxide value.	$E^{1\ p.c.}_{1\ c.m.}$ at 232 mμ	$E^{1\ p.c.}_{1\ c.m.}$ at 270 mμ
B 1	0	0	2·86	5·09
B 2	2	4·8	3·45	4·81
B 3	4	56·5	13·0	3·18
B 4	7	145	22·6	2·04
B 5	10	165	29·0	1·68
B 6	11·5	178	34·3	1·89
B 7	14·5	261	44·1	2·10
B 8	17·5	260	43·8	2·18

DISCUSSION

The highest unsaturated acid present in ground nut oil is linoleic acid, which naturally should be responsible for the conjugation changes observed in the oil with correlation between peroxide value and the concentration of conjugated diene hydroperoxides. Such correlation, however, cannot be extended to groundnut oil since the peroxides are derived from oleate esters as well.

Moreover, Farmer's hydroperoxide theory envisages the formation of both conjugated and unconjugated hydroperoxide from linoleate esters, a suggestion on which later experimental evidences (Gunston and Hilditch, 1946 : Holman and Bergstrom, 1948 : Privet, Lunberg *et al.*, 1946) are not wholly conclusive.

The starting oils, samples A 1 and B 1 in tables A and B, were similar in every other respect except that sample B 1 contains a trace of conjugated triene, from which sample A 1 is free. It is rather significant how this much of triene has influenced the rate of peroxide development. This observation agrees well with that of Gunstone and Hilditch who demonstrated that a trace of methyl linoleate greatly enhances the autoxidation of methyl oleate.

It has been shown elsewhere that treatment with acid treated clays brings about triene conjugation in groundnut oil (Sen Gupta, loc. cit). Fig. 3 shows the same triene conjugation brought about by treatment of the oil with potasium iodide and acetic acid. For this development, the only pre-requisite is that the oil should be partly autoxidised, as no triene development occurs if the oil be completely free from peroxides.

The development of triene conjugation by reduction with potassium iodide and acetic acid would tend to suggest that the clay may also play the same role as a reducing agent. To test the validity or otherwise of such a hypothesis, the clay in water suspension is treated with chlorine gas, to eliminate any reducing groups that may be present. Such chlorine-treated clay, washed and dried, and when tested with a sample of autoxidised oil, brings about the conjugated triene all the same. Thus the possibility of the clay functioning as a reducing agent is ruled out, although the material may bring about reduction catalytically, without itself being oxidised in the process.

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SECTION G

TESTING AND ANALYSIS

A NEW METHOD OF ESTIMATION OF UNSATURATED GLYCERIDES

by G. C. Dey, D. Munshi, D. P. Mukherjee and A. N. Saha

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Natural fats and oils are mixtures of glycerides. Tri-glycerides can be broadly classified as follows: GS_3, GS_2u, GS_1u_2 and Gu_3. Where G represents glycerol residue, S saturated acids, u unsaturated acids. The unsaturated acids may be mono-, di- or tri- ethenoid. The number of carbon atoms also varies both in saturated and unsaturated acids. Most of the fats and oils contain more than one saturated and unsaturated acids. These acids are distributed in glyceride molecules with the result that they from large varieties of glyceride molecules.

The separation of these glycerides or their estimation presents a difficult problem. The first method of estimation of saturated and unsaturated glycerides is due to Hilditch (1927) and his collaborators. The method is based on the oxidisability of unsaturated glycerides in presence of $KMnO_4$. The oxidised product is separated by taking help of their solubility. The method of separation of the oxidised product has been modified by Kartha (1953).

Another method of separation has been attempted by Hilditch *et al.* on the principle of fractional crystallisation at low temperature from solvents.

The saturated and unsaturated acids which form triglycerides in natural fats and oils are separated by two methods. In one, the difference of solubility of metallic salts of saturated and unsaturated acids has been utilised and in the second, help of oxidisability of unsaturated acids is taken. The difference of solubility of Pb-salts has been of great help in separating solid and liquid fatty acids. This fact interested us to examine the solubility of Pb-salts of maleic anhydride adducts of triglycerides of conjugated fatty acids.

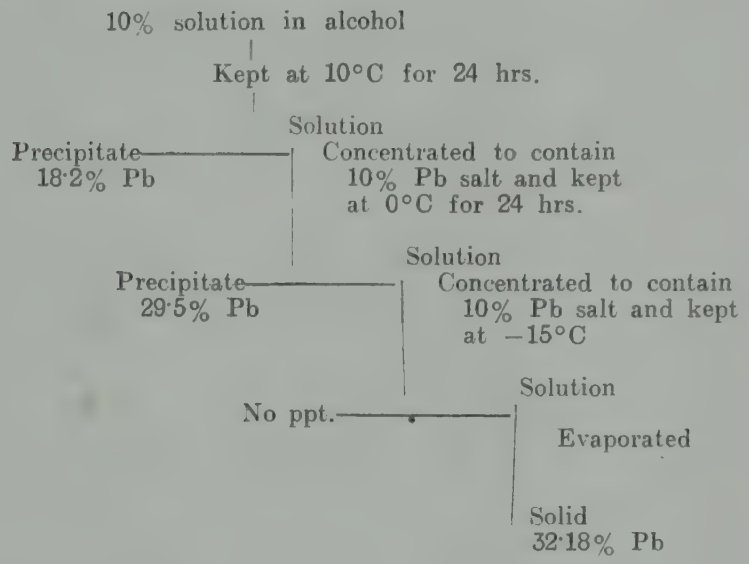
Experimental :

Four charges, each consisting of 3 gms. of tung oil and 25 c.c. of 6 per cent solution of maleic anhydride in toluene were refluxed for 3 hrs. in an oil bath. The flasks were allowed to cool for a few minutes and 5 c.c. of distilled water were added in each flask through the condensor and gently boiled for 15 minutes. After cooling 5 c.c. of ether and 20 c.c. of water were added through the condenser. The contents of the flasks were then transferred into a separating funnel and freed from maleic acid by repeated washing with water.

The solvents were evaporated at reduced pressure. The adduct was neutralised with alcoholic NaOH and alcohol was evaporated off at reduced pressure. The sodium salt thus prepared was dissolved in water and was extracted with petroleum ether to remove the unreacted triglycerides. The sodium salt of the adduct was acidified with dilute HCl and extracted with

ethyl ether. Solvent was evaporated off at reduced pressure and the residue thus obtained was dissolved in minimum quantity of alcohol and was neutralised with standard alcoholic NaOH. From the amount of NaOH consumed, the quantity of Pb-acetate required to form the lead salt was calculated out. Warm alcoholic solution of Pb-acetate was added to hot solution of Na-salt whence Pb-salt precipitated. The Pb-salt was washed free from Na-acetate by water. The Pb-salt thus prepared was dried at 60°C in vacuum.

A ten percent solution of Pb salt was taken and fractional precipitation of the Pb-salt from this solution was done according to the following scheme:—



Discussion of results

A maleic anhydride adduct of a trielaeostearin will combine with three atoms of Pb, that of a dielaeostearin with two and a mono- will combine with one. The respective theoretical Pb content of mono- di-, and trielaeostearic adducts is 17·3, 28·1, and 33·8 per cent. The salts which could be fractionated from alcoholic solutions of Pb-salts contained 18·2, 29·5, and 33·2 per cent Pb respectively. The little variation in lead contents is due to the contamination of mono- with di- and di- with tri- and tri- with di-. 18·2 per cent Pb is little higher than that of the theoretical of the adduct of GS_2u. But the figure suggests that the contamination is not much and tolerable in this type of analytical work. The other two figures show the similar variation.

So, this method day be of use when it is perfected to separate and estimate mono-, di- and tri- glycerides of dienoic and trienoic acids.

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CHROMATOGRAPHIC SEPARATION OF GLYCERIDES AND UNSATURATED FATTY ACIDS

by B. T. R. Iyengar and M. M. Chakrabarty

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Chromatogrphy as applied to fat chemistry is still in the research stage, though its application in other fields has become quite routine. Considerable work has been done in the separation of saturated fatty acids by Kaufmann (1939, 1940), Cassidy (1940, 1941) and Mazumdar and Goswami (1947). Some work has been done on the separation of methyl esters of unsaturated fatty acids by Swift, Gordon, Rose and Jamieson (1943), Reimenschneider, Herb and Nichols (1949), and Hilditch, Patel and Riley (1951. Holman and Williams (1951) found that non-conjugated trienoic acid was adsorbed less strongly than its saturated analogue. whereas conjugated trienoic acid was more strongly adsorbed than its saturated analogue. Abu Nasr and Holman (1954) segregated cod liver oil which contains highly unsaturated acids, though non-conjugated and Holman (1951) applied carrier displacement chromatography both to saturated and unsaturated acids but not to conjugated systems. It appears that no appreciable work has been done with the separation of conjugated unsaturated systems. One of the objects of the present study was to investigate the behaviour of the unsaturated conjugated acids towards chromatographic segregation.

Regarding the segregation of glycerides although in recent years many studies on the glyceride composition of fats have been made with the help of modern methods, the question of the glyceride structure is still open due to chiefly the limitations of the experimental technique. Although, so far it has not been possible to explain all the facts relating to glyceride structure by anyone of the four theories of glyceride distribution, the even distribution theory has been found to be much more applicable in the case of seed fats. Chromatography of glycerides has been attempted before. Walker and Mills (1942, 1943), and Reinbold and Dutton (1948) experimented on linseed and soybean oils respectively. Claesson (1946) and Hamilton and Holman (1954) studied separabilities of model mixtures of glycerides. Most of these works were undertaken before the advent of spectrophotometric and low-temperature solvent crystallisation methods for the determination of unsaturated glycerides. Recently of course Vasudevan Nair and Varier (1956) have studied the segregation of the component glycerides of C. wightianum by chromatographing over a column of alumina with light petroleum ether. It was considered desirable, therefore, to reinvestigate the use of chromatographic technique in the resolution of glycerides particularly with those oils, whose glyceride distribution has been studied by modern techniques other than chromatography. Indian poppy seed oil was chosen for the preliminary work.

Some preliminary work was done in this laboratory to investigate the behaviour of the unsaturated conjugated systems towards chromatographic segregation. In this case the mixed fatty acids obtained from Indian tung oil was used as the source material. The present work also included the study of the segregation of glycerides present in tung oil by elution analysis using silica gel as adsorbent and pet. ether (40-60°) as solvent and finding the suitability of silica gel in the separation of glycerides of conjugated unsaturated fatty acids and other unsaturated and saturated fatty acids. Glycerides of fatty acids containing conjugated unsaturation have not been segregated by by chromatography uptil now. Tung oil contains high percentage of elaeostearic acid (conj. triene acid), linoleic, oleic acid and a small amount of saturated acids. The present work was intended to throw some light on the separability of the glycerides of conjugated and non-conjugated unsaturated acids.

Experimental

1. Preparation of silica gel:—

Silica gel obtained in the market (Protex. Sorb the Davison Chem. Corp. U.S.A.) was used for activation.

The silica gel was ground to pass a 60 mesh (B.S.S.) sieve and retained on 200 mesh (B.S.S.). This was treated with conc. HCl, washed repeatedly with hot water and dried. The resultant product was activated for 2-2½ hrs. at 250°C and kept in a flask in inert atmosphere until used. The chromato graphic column was set set up in the usual manner by the wet slurry method by continuous tamping, care being taken that no air gaps are formed, which may cause channeling during the course of the experiment. The solvents used in all the experiments was petroleum ether (40-60) and diethyl ether in different proportions.

The first part of the work consisted in the study of the separation of the conjugated unsaturated fatty acid present in a sample of tung oil. After the mixed fatty acid from a sample of Indian tung oil was liberated by the usual method, it was esterified with pure methanol, using dry RCl gas as the catalyst. The ester which separated on standing was extracted with petroleum ether, washed with alkali and finally with water after which the solvent was removed completely under vacuum. The characteristics of the methyl ester of the mixed fatty acids determined by standard methods are given in Table I.

TABLE I

Analysis of methyl esters of mixed fatty acids of tung oils used for the three experiments.

Experiment	I	II	III
Iodine value. Benham & Klee's method (1950)	—	—	196·6
Iodine value (Wij's 30 mins.) ...	142·8	140·8	—
From spectrophotometric analysis, linoleate %	—	—	17·80
.. elaeostearate %	64·16	61·90	55·47

The comparative results of the three experiments are given in Table II, and the details of each run are given in Tables III, IV and V respectively.

TABLE II

	Expt. I	Expt. II	Expt. III
Adsorbent used	Silica+hyflo supercel (80 : 20 by weight)		
Amount of adsorbent (gms)	360	270	275
Height of packing (cms)	55	40	40
Particle size of silica (B.S.S. mesh) ...	−60, +150	−60, +150	−60, +150
Method of packing	Slurry packing		
Rate of flow of solvent	One litre per six hours		
Weight of methyl ester subjected to adsorption analysis (gms)	12·3034	11·0836	12·3271
Weight of methyl ester eluted	12·2815	11·0782	12·2991
Percentage of recovery	99·84	99·97	99·70
Percentage of elaeostearate recovered ...	87·20	74·79	71·89
Percentage of linoleate recovered ...	—	—	92.60
(Based on the elaeostearate content of the amount of material subjected to adsorption analysis)			
Percentage of elaeostearate recovered ...	87·7	74·86	72·10
Percentage of linoleate recovered	—	—	92·20
(Based on the total amount of material recovered on elution)			
Highest methyl elaeostearate content obtained (%)	87·18	75·85	70·55
Percentage enrichment of elaeostearate over original ester	23·02	13·95	15·08

TABLE III
(Experiment I)

Fraction	Vol. eluant (ml)	Eluant	Wt. of fraction gms)	I.V. (Wij's)	Methyl Elaeostearate % in fraction	Wt. in (gms)
1	3500	Petro ether (40-60°C)	1·2462	68·63	0·9821	·01249
2	1500	,,	1·3858	87·3	14·40	·1992
3	1000	,,	·8320	145·4	65·42	·5443
4	1000	,,	·8050	177·3	87·18	·7018
5	1000	,,	·5256	164·3	76·06	·4004
6	1200	,,	·6146	144·4	64·86	·3987
7	1400	,,	·9300	134·8	60·70	·5645
8	1000	,,	·5560	165·1	76·36	·4245
9	2000	,,	·9726	172·2	86·16	·8496
10	1000	,,	·8206	170·3	85·16	·6987
11	1000	,,	·6668	148·3	69·57	·4638
12	1000	Petr. ether + 20% diethyl	1·1086	167·5	82·75	·9175
13		,,	·2140	92·1	19·38	·4148
14		Petr. ether + 50% diethyl	·8852	84·4	6·32	·05598
15	500	100% diethyl ether	·7185	74·0	5·12	·03685

TABLE IV
(Experiment II)

Fraction	Vol. Eluant (ml.)	Eluant	Wt. of fraction (gms)		Methyl Elaeostearate % in fraction	Wt. in (gms)
1	1400	Petr. ether 40°-60°C	2·0680	87·16	13·90	·2875
2	1400	,,	3·5690	150·4	75·85	2·505
3	1000	,,	1·5520	160·8	70·20	1·177
4	1000	,,	·4220	135·4	60·72	·2563
5	1000	,,	·3984	115·2	35·13	·1400
6	2000	,,	·5724	102·2	26·05	·1491
7	3500	,,	·2908	122·8	45·80	·1331
8	1000	P. ether + 20% diethyl ether	·6730	154·1	72·86	·4904
9	2000	,,	·3200	92·5	16·06	·0514
10	2000	P. ether + 50% diethyl ether	·6066	87·02	6·42	·0389
11	1000	100% diethyl ether	·6060	86·26	6·01	·0360

TABLE V

(Experiment III)

Fraction	Vol. eluant (ml.)	Eluant	Wt. of fraction (gms)	I. V. Benham & Klee's	Methyl Elaeostearate % in fraction	Wt. in gms.	% Methyl in fraction	Linoleate Wt. in gms.	Ref. index at 40°C
1	750	Petr. ether (40°-60°C)	1·6013	64·8	0·31	·0050	15·5	0·2480	1·4445
2	750	,,	2·3977	143·9	39·12	·9536	16·99	·3621	1·4830
3	750	,,	1·3040	149·5	45·93	·5980	11·40	·1430	1·4910
4	750	,,	0.4659	143·5	37·71	·1758	10·50	·0459	—
5	750	,,	·2473	226·9	56·63	·1411	—	—	1·4970
6	750	,,	·2931	231·5	63·49	·1862	14·75	·0432	—
7	750	,,	·5565	236·2	64·79	·3605	19·72	K·1097	1·4970
8	1000	,,	·9511	252·5	65·22	·6185	34·78	·3308	1·5040
9	1000	,,	·3204	256·7	67·64	·2142	32·36	·1010	1·5050
10	1000	,,	·4320	261·3	70·55	·3035	29·45	·1272	1·5100
11	1000	,,	·2931	210·5	50·02	·1456	19·50	·0571	1·4900
12	1000	,,	·2505	170·5	35·38	·1278	16·05	·0421	1·4795
13	1000	,,	·1900	150·5	25·75	·0500	—	—	—
14	1000	P. ether + 5% diethyl ether	·6250	240·5	64·20	·3968	10·85		1·4970
15	1000	,,	·4905	245·5	65·90	·3234	12·00		1·4975
16	1000	,,	·2758	180·5	41·93	·1134	15·21		—
17	1000	P. ether + 20% diethyl ether	·4779	138·5	15·00	·0720	21·02	·1004	1·4625
18	1000	P. ether + 50% diethyl ether	·6010	122·5	10·85	·0667	22·98	·1381	1·4600
19	1000	P. ether + 75% diethyl ether	·2312	84·7	7·00	·0162	9·50	—	—
20	1000	100% diethyl ether	·3938	83·2	5·95	·0240	4·75	·0187	—

It would be evident from the above results that activated silica gel along with hyflo-supercel (80:20) constituted a fairly good medium for selective adsorption of conjugated acids. From the graph which can be plotted with percentage methyl elaeostearate against effluent volume it is clear that the behaviour of methyl elaeostearate during selective adsorption is similar to that of methyl linoleate under identical conditions as was shown by Hilditch *et al.* It has also been demonstrated that enrichment of elaeostearic acid by this technique is possible and that column height has a direct bearing on the percentage of enrichment. Thus it can be seen that percentage enrichment using 40 cm. column height, is of lower order than that using 55 cm. The recovery of eluted methyl esters is satisfactory, although the pronounced chemical activity of the elaeostearate created hindrances by formation of polymeric oxidation and constituted thereby a substantial loss of elaeosterate. Further work, to correlate the influence of different variables as also, study further for the possibilities of enrichment of other conjugated dienoic, trienoic and tetraenoic acids is in progress.

Regarding the second part of the work which consisted in the study of the segregation of the glycerides from poppy seed oil, the same technique and procedure as above was adopted. The oil was obtained from a commercial sample of Indian poppy seeds by extraction with petrol ether (40-60) and neutralised with alkali before the experiment. The mixed fatty acids of the oil were analysed by the spectrographic technique of Hilditch *et al.* The results and the characteristics of the oil determined by standard methods are given in Table VI.

TABLE VI

Analysis of oil sample (Indian poppy seed oil)

Iodine value (Wij's 30 min.)	136·2
Saponification equivalent	294·2
Analysis of mixed fatty acids :—	
Iodine value (Wij's 30 min.)	141·7
From spectrophotometric measurements :—	
Linoleic acid	63·48%
Oleic acid	29·41%
Saturated (by. diff.)	7·11%

Details of the column and results are given in Table VII.

TABLE VII

Adsorbent used	—Silica gel—Hyflosupersel (80 : 20)
Height of packing	—50 cm. (Diam. 3·5 cm.)
Amount of adsorbent	—345 gms.
Method of packing	—Slurry packing.
Eluant used	—Petroleum ether and diethyl ether in different proportions.
Rate of flow of eluant	—250 c.c./2 hrs.
Weight of poppy oil taken	—17·9447 gms.

Fraction	Vol. of Eluant (ml.)	Eluant	Wt. of fraction (g)	Iodine value (Wij's)
Original oil		—	17·9447	136·15
1	3000	Petr. ether	0·1521	116·6
	500	—do— + 1% diethyl ether		
2	500	Petr. ether + 2% diethyl ether	3·7412	116·8
3	250	,,	3·6283	126·1
4	250	,,	0·9561	132·1
5	250	,,	1·0463	140·6
6	250	,,	0·6513	142·6
7	250	,,	0·9853	151·7
8	250	,,	0·4921	154·1
9	250	,,	0·5063	158·1
10	250	,,	0·5679	159·7
11	500	,,	0·3743	160·4
12	500	,,	0·3978	160·6
13	500	,,	0·2912	166·1
14	500	,,	0·2588	167·8
15	500	,,	0·1458	168·5
16	500	,,	0·1026	156·1
17	500	P. ether + 25% diethyl ether	0·3462 (coloured)	115·3
18	500	,,	0·3188	114·8 (coloured)
19	500	,,	0·1893	113·3
20	500	P. ether + 50% diethyl ether	0·3229	113·3
21	500	,,	0·2420	109·5
22	500	,,	0·1093	109·5
23	500	100% diethyl ether	0·3753	104·6
24	500	,,	0·3500	104·6

Total weight of fraction = 16·5472 gms.
Per cent recovery = 92·3%

Although it has not been possible in the preliminary work to analyse the fractions separated by chromatography, the indications from the difference in iodine values of the earlier and later fractions point out considerable resolution. From the original iodine value of 136.2, fractions having i.v. of the order of 160-169 have been obtained. The iodine value of pure trilinolein is 173·5. It is obvious therefore, that it will not be impossible to separate pure trilinolein in this manner. Of course a better picture will emerge only after the full glycerides composition is computed from these mixtures. Further work is being done in this direction.

Separability of the glycerides of conjugated fatty acids from those of non-conjugated seemed to provide a promising field of investigation and hence the work was taken up, with the object of applying the same selective adsorption technique as used above.

The oil used was a sample of Indian tung oil, which was weighed and dissolved in petroleum ether so as to make 10% solution roughly.

The iodine value and spectrophotometric determinations were carried out on the eluted fractions. The spectrophotometric determination was carried

out directly with the oil with a Beckmann Spectrophotometric according to the standard methods of Hilditch, Morton and Riley.

Details of the experimental procedure and results are given below.

TABLE VIII

Fraction number	Volume of eluate (ml.)	Eluant used	Wt. of fraction	I. V. of fraction
1	6000	P. ether (40-60)	·6086	130·4
2	1000	,,	·4202	145·2
3	1000	10% ether + p. ether	2·8134	150·1
4	1500	,,	1·8925	148·6
5	1500	20% ether + p. ether	1·8925	159·8
6	1500	,,	·8346	168·5
7	2000	50% ether + p. ether	1·7816	145·9
8	2500	,,	·8654	126·6
9	1500	Pure ether	1·1165	100·4
10	2000	,,	·3824	—
			11·7947	

Wt. of tung oil take = 11·98 gms.
Percent recovery = 98·44

TABLE IX

Fraction number	Wt. of fraction	% Elaeostearic acid in tung oil fraction	% Elaeostearic acid as percent of total fatty	Amount of elaeostearic acid in the oil fraction
1	·6086	42·12	44·03	2·2564
2	·4202	50·85	53·16	·2136
3	2·8134	56·92	59·51	1·6020
4	1·0795	53·25	55·67	·5748
5	1·8925	63·03	65·89	1·1930
6	·8346	70·95	74·16	·5921
7		52·32	54·70	·9322
8		47·56	49·72	·4115
9	1·1165	38·20	39·04	·4275
10	·3824	26·45	27·65	·1012
				6·3043

From the above tables it is seen that the percentage of elaeostearic acid increases gradually from fraction 1-6. The glyceride components of the oil containing greater percentages of elaeostearic acid were more strongly adsorb than other components. From fraction of the percentages of elaeostearic acid in the fractions decreased sharply. The lower percentages of elaeostearic acid in those fractions and the colour showed that formation of polymerised product was gradually increasing. The amount of polymerised product formed was determined by the material balance of elaeostearic acid. The recovery of elaeostearic acid was only 88% whereas recovery of the oil was 98.4 per cent. Thus 10·44 per cent of elaeostearic acid was unaccounted for possibly due to polymerisation.

Percentage of elaeostearic acid in fraction 1 was only 42%. It means that in most of the glyceride molecules of that fraction, elaeostearic acid only satisfied one functional group. The 6th fraction contained 70·95 per cent elaeostearic acid. Therefore some amount of trielaeostearin was present in that fraction. The major portion of the fractions was dielaeostearin mono-other acid (linoleic, oleic, or satd.) as the percentage of elaeostearic acid in most of the fractions were 50-65. It was also observed from the experimental results that increased conjugation increases absorption, in keeping with previous experimental work done with conjugated fatty acids on Darco G-60.

From the results, it was found that segregation of glycerides of fatty acids containing conjugated and non-conjugated unsaturation and satd. fatty acids is possible by using selective adsorption technique. Although the percentage of elaeostearic acid in tung oil used is 59·9 per cent, some amount of trielaeostearic was also present. The major portion of the oil found to be dielaeostearin mono-other acid indicates that the glycerides present in tung oil obey the 'rule of even distribution'. The present work was qualitative rather than quantitative. Here, only the percentages of triene conjugated acid in different fractions were determined. If all the fractions were analysed for their linoleic (by spec.) saturated (Bertram's oxidation method) and oleic (by difference) content also, then it would been possible to get a more accurate idea of distribution of glycerides.

The nature of the results obtained however indicates that further work in these lines is likely to yield a more comprehensive information as regards the glyceride structure of natural oils and fats.

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